NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS | REGISTRATION NUMBER

CHEMISTRY

Paper 1 Multiple Choice

9729/01
23 September 2025
1 hour

Additional Materials: Optical Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.
There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.
Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

__Instructions on how to fill in the Optical Mark Sheet__
Shade the index number in a 5 digit format on the optical mark sheet:
2nd digit and the last 4 digits of the Registration Number.

Example:

Student	Examples of Registration No.	Shade:

This document consists of **16** printed pages.

BP~139

BP~140

Answer Key for P1 (MCQ)

1	A	6	C	11	C	16	C	21	C	26	D
2	D	7	C	12	C	17	B	22	A	27	C
3	A	8	C	13	B	18	D	23	D	28	C
4	B	9	B	14	B	19	C	24	C	29	C
5	B	10	D	15	A	20	C	25	C	30	A

1 Sodium chromate(VI), Na_2CrO_4, is manufactured by heating chromite, $FeCr_2O_4$, with sodium carbonate in an oxidising atmosphere. Chromite contains $Cr_2O_4^{2-}$ ions.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

What happens in this reaction?

A Chromium and iron are the only elements oxidised.

B Chromium, iron and carbon are oxidised.

C Only chromium is oxidised.

D Only iron is oxidised.

Ans: A
Reactants: **$FeCr_2O_4$** (Fe = +2 and Cr = +3), Na_2CO_3 (C = +4), O_2 (O = 0).
Products: Fe_2O_3 (Fe = +3), Na_2CrO_4 (Cr = +6), CO_2 (C = +4).
Changes:
Fe: +2 → +3 (**oxidised**)
Cr: +3 → +6 (**oxidised**)
C: +4 → +4 (**no change**)
O: 0 → −2 (**reduced**)
So, only Fe and Cr are oxidised.

2 Which species has two unpaired electrons?

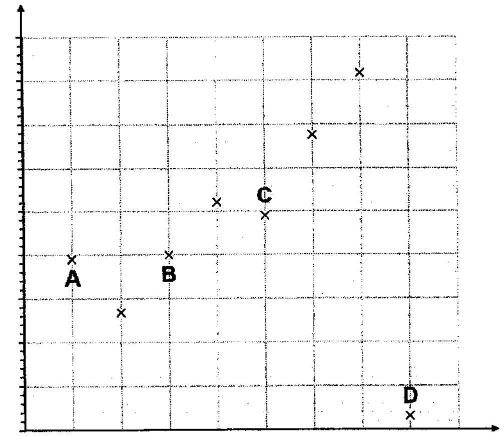
A B^+ **B** Cu^+ **C** Mg **D** S

Ans: D

B^+: $1s^2\ 2s^2$	No unpaired electrons
Cu^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$	No unpaired electrons
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$	No unpaired electrons
S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	2 unpaired 3p electrons

3 **The variation in the second ionisation energy of eight consecutive elements in the Periodic Table with atomic numbers ≤ 20 is shown in the graph.**

Which element is a Group 13 element?



Ans: A

The large drop in 2nd I.E. shows that **D^+** ion has the ns^1 electronic configuration. Hence, the electronic configuration of element **D** is ns^2 and belongs to Group 2. Since the graph is showing consecutive elements in the Periodic Table, the configuration of the other elements can be derived.

A – Group 13
B – Group 15
C – Group 17
D – Group 2

4 What do the ions $^{15}N^{3-}$ and $^{14}C^{4-}$ have in common?

A They have 10 neutrons in their nuclei.

B They have more electrons than neutrons.

C They have a valence electronic configuration of $3s^2\ 3p^6$.

D They contain the same number of nucleons in their nuclei.
Ans: B

species	$^{15}N^{3-}$	$^{14}C^{4-}$
number of protons	7	6
number of neutrons	8	8
number of electrons	10	10
number nucleons	15	14
valence electron configuration	$2s^2\ 2p^6$	$2s^2\ 2p^6$

5 What is the order of decreasing enthalpy change for the three reactions shown?

$$Rb^+(g) \longrightarrow Rb^{2+}(g) + e^- \qquad \Delta H_1$$

$$Br^-(g) \longrightarrow Br(g) + e^- \qquad \Delta H_2$$

$$Kr(g) \longrightarrow Kr^+(g) + e^- \qquad \Delta H_3$$

A $\Delta H_1 > \Delta H_2 > \Delta H_3$

B $\Delta H_1 > \Delta H_3 > \Delta H_2$

C $\Delta H_2 > \Delta H_1 > \Delta H_3$

D $\Delta H_2 > \Delta H_3 > \Delta H_1$
Ans: B

All 3 equations are for ionisation energy.
Rb^+, Br^- and Kr are isoelectronic with 36 electrons.
Nuclear charge increases from $Br^- < Kr < Rb^+$ while shielding effect remains constant.
Nuclear attraction for the most loosely held electron increases from $Br^- < Kr < Rb^+$.
Largest amount of energy is required to remove the most loosely held electron from Rb^+.

6 Barium dithionate, $BaS_2O_6.2H_2O$, is soluble in water.

$S_2O_6^{2-}$ ions slowly decompose in acidic solution.

$$S_2O_6^{2-}(aq) \longrightarrow SO_2(g) + SO_4^{2-}(aq)$$

3.513 g of $BaS_2O_6{\bullet}2H_2O$ is dissolved in some water and the solution made up to the mark with HC*l*(aq) in a 100 cm^3 volumetric flask.

At time *x* min, a white precipitate of mass 0.661 g is present in the flask.

What is the concentration of BaS_2O_6 in the volumetric flask at time *x* min?

[A_r: Ba, 137.3; S, 32.1; O, 16.0; H, 1.0]

A 0.0077 mol dm^{-3}

B 0.0090 mol dm^{-3}

C 0.077 mol dm^{-3}

D 0.090 mol dm^{-3}
Ans: C

Amount of $BaS_2O_6.2H_2O = \frac{3.513g}{(137.3+32.1\times2+16.0\times6+18.0\times2)} = 0.01053\ mol$

The white ppt is $BaSO_4$.
Amount of $BaSO_4 = \frac{0.661g}{(137.3+32.1+16.0\times4)} = 0.002831\ mol$

Amount of BaS_2O_6 at x min = 0.01053 – 0.002831 = 0.007698 mol

$[BaS_2O_6]$ at x min $= \frac{0.007698}{\frac{100}{1000}} = 0.077$ mol dm^{-3}

BP~141

7 $NH_4Fe(SO_4)_2 \cdot 12H_2O$ is a hydrated 'double salt'. A student analyses this double salt using the following chemical tests.

Which row gives the correct result for the stated test?

	Test	Results
1	Reaction with cold NaOH(aq)	Green ppt
2	Reaction with $Ba(NO_3)_2$(aq)	White ppt
3	Reaction with warm NaOH(aq)	Red-brown ppt and an alkaline gas

A 1, 2 and 3 **B** Only 1 and 2 **C** Only 2 and 3 **D** Only 1

Ans: C

In the double salt, oxidation state of Fe is +3.
1 is a wrong result. With cold NaOH(aq), $Fe(OH)_3$ red-brown ppt is formed.
2 is a correct result. $BaSO_4$ white ppt is formed.
3 is a correct result. With warm NaOH(aq), as NH_4^+ is present, NH_3 gas will be given off. At the same time, $Fe(OH)_3$ red-brown ppt is formed.

8 Which statements about BF_3 and NF_3 are correct?

1 The shape of BF_3 is trigonal planar while that of NF_3 is trigonal pyramidal.

2 Both BF_3 and NF_3 are polar molecules.

3 BF_3 can act as a Lewis acid because the boron atom has empty low-lying orbitals.

A 1 and 2 **B** 2 and 3 **C** 1 and 3 **D** 1, 2 and 3

Ans: C

Statement 1: Shapes
- **BF_3**: central B, 3 bonding pairs, 0 lone pairs → **trigonal planar.**
- **NF_3**: central N, 3 bonding pairs, 1 lone pair → **trigonal pyramidal.**
  So statement **1 is correct.**
-

Statement 2: Polarity
- **BF_3**: although each B–F bond is polar, the **symmetry (trigonal planar)** cancels dipoles → **non-polar molecule.**
- **NF_3**: asymmetric, lone pair on N, net dipole → **polar molecule.**
  So statement **2 is incorrect** (only NF_3 is polar).

Statement 3: Lewis acidity
BF_3: central B has an **empty 2p orbital (low-lying, energetically accessible)** → can accept lone pair electron from a donor.
So statement **3 is correct.**

9 Silicon carbide has a similar structure to diamond.

Silicon carbide can be used as

A a lubricant.

B a tip for cutting tools.

C a substitute for pencil 'lead'.

D an electrical conductor.

Ans: B

Diamond: each sp^3 hybridised C atom forms strong covalent bond with 4 other C atoms in a tetrahedral arrangement in the giant covalent lattice structure. Properties of diamond include: very high melting point, non-electrical conductor, hard, insoluble in all solvents.

10 Which statement is **not** a basic assumption of the kinetic theory of gases?

A The atoms or molecules have negligible size in comparison with the space they occupy.

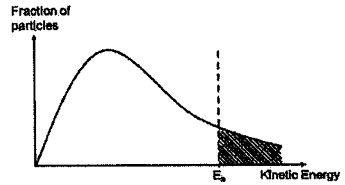
B There are negligible intermolecular forces between the gas particles.

C Collisions between the individual particles and the vessel are perfectly elastic.

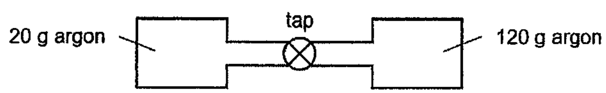
D The particles of a given gas have the same kinetic energy at a given temperature.

Ans: D

The particles of a given gas do not have the same kinetic energy at a given temperature, in fact, they have a range of kinetic energies, as represented in the Boltzmann distribution curve.



11 The diagram below shows two containers of argon gas connected by a closed tap. Each container has a volume of 500 dm^3.



The temperature of the system is changed to 250 °C and the tap is opened.

What is the pressure of argon within the system at 250 °C?

A 7.29 kPa **B** 14.6 kPa **C** 15.3 kPa **D** 30.5 kPa

Ans: C

Total no. of mol of Ar = $\frac{20}{39.9} + \frac{120}{39.9}$ = 3.509 mol
Final volume (both 500 dm^3 vessels connected) = 1000 dm^3 = 1 m^3
Final Temperature, T = 250 + 273 = 523K
Apply pV=nRT

$P = \frac{nRT}{v} = \frac{3.509 \times 8.31 \times 523}{1}$ = 15 251 Pa = 15.3 kPa (3 s.f.)

12 The standard enthalpy change of combustion of but-1-ene, $CH_2=CHCH_2CH_3(g)$, is x kJ mol^{-1}.

The standard enthalpy change of the reaction $2C_2H_4(g) \longrightarrow CH_2=CHCH_2CH_3(g)$ is y kJ mol^{-1}.

What is the standard enthalpy change of combustion of ethene, $C_2H_4(g)$?

A $\frac{x}{2} + y$ kJ mol^{-1}

B $x + \frac{y}{2}$ kJ mol^{-1}

C $\frac{x+y}{2}$ kJ mol^{-1}

D $\frac{x\ y}{2}$ kJ mol^{-1}

Ans: C

$\Delta H_r = 2(\Delta H_c\ C_2H_4) - \Delta H_c\ CH_2=CHCH_2CH_3$
$y = 2(\Delta H_c\ C_2H_4) - x$
$\Delta H_c\ C_2H_4 = \frac{x+y}{2}$ kJ mol^{-1}

[Turn over

13 Which suggested mechanism is consistent with the experimentally-obtained rate equation?

	rate equation	suggested mechanism
A	rate = $k[N_2O][H_2]$	$2NO + H_2 \longrightarrow N_2O + H_2O$ $N_2O + H_2 \xrightarrow{slow} N_2 + H_2O$
B	rate = $k[NO]^2[H_2]^2$	$2NO + H_2 \longrightarrow N_2O + H_2O$ $N_2O + H_2 \xrightarrow{slow} N_2 + H_2O$
C	rate = $k[H_2O_2][I^-]$	$H_2O_2 + I^- \longrightarrow IO^- + H_2O$ $H_2O_2 + IO^- \xrightarrow{slow} I^- + H_2O + O_2$
D	rate = $k[H_2O_2][IO^-]$	$H_2O_2 + I^- \longrightarrow IO^- + H_2O$ $H_2O_2 + IO^- \xrightarrow{slow} I^- + H_2O + O_2$

Ans: B

For A and D, N_2O and IO^- are intermediates so they cannot appear in the rate equation.
For C, the rate equation in the option is for the first step but the first step is not the slow step.
Hence A, C and D are wrong.
For B, rate = $k[N_2O][H_2]$ since the second step is the slow step. N_2O is formed from the first step and it involves 2NO and 1H_2, hence the rate equation after substituting N_2O as 2NO and 1H_2 is rate = $k[NO]^2[H_2]^2$.

BP-143

14 Propanone reacts with iodine in the presence of sulfuric acid.

$$CH_3COCH_3\,(aq) + I_2\,(aq) \longrightarrow CH_3COCH_2I\,(aq) + HI(aq)$$

The rate equation for this reaction is: rate = $k[H^+][CH_3COCH_3]$.

Two experiments were carried out. In both experiments, the initial concentrations of propanone and iodine remained the same but the initial concentration of the sulfuric acid was changed. The initial rate in the first experiment was three times faster than the initial rate in the second experiment. In the first experiment the initial pH was 1.50.

What is the initial pH in the second experiment?

A 1.02 **B** 1.98 **C** 2.28 **D** 4.50

Ans: B

As conc of propanone is kept constant,

$\frac{rate\ (1)}{rate\ (2)} = \frac{k(10^{-1.50})}{k\,[H^+]}$

$\frac{3}{1} = \frac{(0.03162)}{[H^+]}$

$[H^+] = 0.01054$ mol dm^{-3}

pH = – lg 0.01054 = 1.977 ≈ 1.98

15 Which factor contributes to $Ba(NO_3)_2$ decomposing at a higher temperature than $Mg(NO_3)_2$?

A The charge density of the Ba^{2+} ion is lower than that of the Mg^{2+} ion.

B The standard enthalpy change of formation of BaO is more negative than that of MgO.

C The lattice energy of $Ba(NO_3)_2$ is less negative than that of $Mg(NO_3)_2$.

D The melting point of $Ba(NO_3)_2$ is higher than that of $Mg(NO_3)_2$.

Ans: A

A. The charge density of the Ba^{2+} ion is lower than that of the Mg^{2+} ion.

✓ Correct. This means Ba^{2+} polarises the NO_3^- ion less → nitrate is more stable → requires higher temp to decompose.

B. The standard enthalpy change of formation of BaO is more negative than that of MgO.

✗ Wrong. In fact, ΔHf of MgO is more negative (more exothermic) than BaO because Mg^{2+} has higher charge density. This option does not explain the trend in nitrate stability.

C. The lattice energy of $Ba(NO_3)_2$ is less negative than that of $Mg(NO_3)_2$.

✗ True statement, but not the controlling factor for *thermal stability of the nitrate*. Lattice energies relate more to ionic size and packing, not directly to decomposition temperature.

D. The melting point of $Ba(NO_3)_2$ is higher than that of $Mg(NO_3)_2$.

✗ Irrelevant. Melting point is not the reason for differences in thermal stability of nitrates.

16 Which statement explains the trend of decreasing volatility from HC*l* to HI?

A The electronegativity between the bonded atoms increases.

[Turn over

B The molecules are polar and they have increasingly stronger permanent dipole-permanent dipoles.

C There are more electrons in iodine atom than in chlorine atom.

D The bond length decreases from H–C*l* to H–I, hence thermal stability increases.

Ans: C

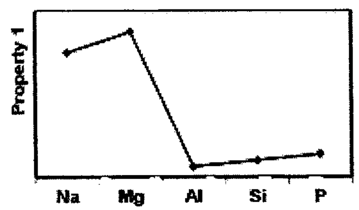
Decreasing volatility means increasing boiling point / stronger intermolecular forces of attraction.

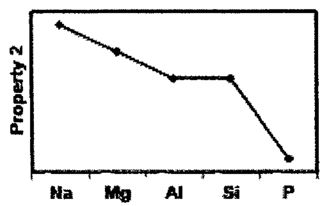
The difference in electronegativity between the H and the halogen decreases from HC*l* to HI, i.e. HI is the least polar and hence the pd-pd between H I is the weakest. This does not help to explain the trend.

Instead, the size of electron cloud increases from HC*l* to HI, resulting in stronger instantaneous dipole-induced dipole interactions (id-id) which help to explain the trend.

The covalent H-X bonds are not broken during boiling, so option D is irrelevant.

17 The graphs below show the variation of two properties of some Period 3 elements and/or their compounds.





Which option correctly describes properties 1 and 2?

	Property 1	Property 2
A	atomic radius of the elements	electrical conductivity of the elements
B	boiling point of the chlorides at the highest oxidation states	pH of the oxides when added to water
C	melting point of the oxides	first ionisation energies of the elements
D	electrical conductivity of elements	pH of the chlorides at the highest oxidation states when added to water

Ans: B

For option A

Property 1 **<u>cannot be atomic radii</u>** as it should be a **<u>continuous decrease across the period</u>** due to increase in nuclear attraction for the outermost electron. This is because of increase in nuclear charge but constant shielding caused by the same number of inner electrons.

Property 2: **<u>Electrical conductivity should increase from Mg to Al</u>** due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.

For option B

Boiling point of chloride compounds decreases from NaCl to $AlCl_3$ as $AlCl_3$ is a simple covalent molecule therefore easier to overcome the intermolecular temporary dipole induced dipole than ionic bonds in giant ionic lattice of NaCl and $MgCl_2$.
From $AlCl_3$ to PCl_5, they have the structure of simple covalent molecules with Mr of $AlCl_3$ (133.5) < $SiCl_4$ (170.1) < PCl_5 (208.5). B.pt increases with increasing ease of distortion of the electron cloud of the chloride compound.

Hence property1 shows the correct trend in the b.pt of chlorides across period 3 element.

Property 2: **acid base property of oxide** depends on the **nature of bonds present in the oxide** compound. While ionic oxide tends to be basic and covalent oxide is acidic; ionic oxides with significant covalent character will be amphoteric, this is usually observed when cation has high charge/size ratio.

pH of oxides in aqueous medium not only depends on the nature of the bonds, **solubility** also matters.

Na_2O is **basic and fully soluble** in water, therefore pH very high (highly alkaline).
Solubility of MgO less than Na_2O but more than Al_2O_3, hence pH of MgO > Al_2O_3.
pH of Al_2O_3 and SiO_2 are both equal to 7 because both are insoluble in water but Al_2O_3 is an amphoteric oxide while SiO_2 is an acidic oxide.
Oxides of P dissolves in water to give phosphoric acid therefore pH is very low.

Hence property 2 shows the correct trend for pH of aqueous oxides across period 3.

For option C

Melting points of oxides across the period should peak at SiO_2 since it has a very strong giant covalent lattice.
Phosphoric oxide is a simple covalent molecule, therefore there should be a drastic drop of m.pt from SiO_2 to P_4O_{10}.
Hence property 1 cannot be m.pt of oxides across period 3 elements.

First ionisation energy of elements across period should exhibit a general increasing trend due to increasing nuclear attraction for the most loosely held electron. This is due to increase in nuclear charge but constant shielding effect by the same number of inner shell electrons.

Hence property 2 cannot be first ionisation energy.

For option D

Electrical conductivity should increase from Na to Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.

For chlorides across period 3 element, they are all soluble in aqueous medium. For chlorides that dissociates into ions in aq medium, cation hydrolysis gives rise to acidic solution. Extent of cation hydrolysis increases with charge/size ratio of the cation. Hence $AlCl_3$ (aq) more acidic than $MgCl_2$(aq) while NaCl is neutral (pH =7)

On the other hand, covalent chlorides react with water to form HCl therefore the pH value should be low for both $SiCl_4$ and PCl_5.

Hence graph of property 2 does not agree with the pH trend of aqueous chlorides across the period.

18 10.0 cm^3 of 0.100 mol dm^{-3} of dilute sodium hydroxide was titrated against 0.100 mol dm^{-3} of dilute ethanoic acid.

What is the volume of dilute ethanoic acid required to produce a buffer with maximum buffering capacity?

A 5.00 cm^3 **B** 10.00 cm^3 **C** 15.00 cm^3 **D** 20.00 cm^3

Ans: D

In this case, the buffer formed should contain a mixture of weak ethanoic acid and its ethanoate conjugate base. Excess ethanoic acid must be added to produce a buffer, making option **A** and **B** incorrect.

V_{eqv} = 10.0 cm^3 (reaction involved a monobasic acid and a monobasic base with the same concentration).

Since maximum buffer capacity occurs when the concentration of ethanoic acid and the ethanoate conjugate base, $2V_{eqv}$ = 20.0 cm^3 of ethanoic acid must be added.

BP-145

BP~146

19 An acidified solution contains $CaCl_2$, $FeCl_2$ and $MnCl_2$, each of concentration 0.10 mol dm^{-3}. Carbon dioxide is blown through the solution until it is saturated with carbon dioxide at 25 °C. The concentration of CO_3^{2-}(aq) in the saturated solution reaches 1×10^{-9} mol dm^{-3}.

The value of the solubility product, K_{sp}, of each of the carbonates at 25 °C is given below.

$CaCO_3$	3.8×10^{-9} mol^2 dm^{-6}
$FeCO_3$	3.2×10^{-11} mol^2 dm^{-6}
$MnCO_3$	2.5×10^{-13} mol^2 dm^{-6}

Which statement describes what happens in the solution?

A Only $CaCO_3$ and $FeCO_3$ are precipitated.

B Only $CaCO_3$ is precipitated.

C Only $MnCO_3$ and $FeCO_3$ are precipitated.

D Only $MnCO_3$ is precipitated.
Ans: **C**

Ionic product of $MCO_3 = [M^{2+}][CO_3^{2-}] = (0.1)(1\times10^{-9}) = 1\times10^{-10}$ mol^2dm^{-6}

Since ionic product > K_{sp} of $FeCO_3$ and K_{sp} of $MnCO_3$, ppt of $FeCO_3$ and $MnCO_3$ will be formed.

Since ionic product < K_{sp} of $CaCO_3$, $CaCO_3$ will be soluble.

20 Buta-1,2-diene and but-2-yne both have the same molecular formula, C_4H_6. They exist in equilibrium as shown:

$$\underset{\text{buta-1,2-diene}}{CH_2{=}C{=}CHCH_3} \rightleftharpoons \underset{\text{but-2-yne}}{CH_3C{\equiv}CCH_3}$$

Which bond is present in buta-1,2-diene but **not** present in but-2-yne?

A a σ bond formed by s – sp overlap

B a π bond formed by p – p overlap

C a σ bond formed by sp – sp^2 overlap

D a σ bond formed by sp^2 – sp^2 overlap
Ans: **C**

Buta-1,2-diene hybridisation:	$CH_2{=}C{=}CHCH_3$ sp^2 sp sp^2 sp^3
but-2-yne hybridisation:	$CH_3C{\equiv}CCH_3$ sp^3 sp sp sp^3

A	a σ bond formed by s – sp overlap: not present in both molecules
B	a π bond formed by p – p overlap: present in both molecules
C	a σ bond formed by sp – sp^2 overlap: C-C in butadiene, not in but-2-yne
D	a σ bond formed by sp^2 – sp^2 overlap : not present in both molecules

21 The chlorofluorocarbon, CCl_2F_2, can cause the breakdown of ozone in the upper atmosphere.

Which initiation step could occur with ultraviolet radiation to catalyse this breakdown?

A $CCl_2F_2 \rightarrow$ •C + •Cl_2F_2

B $CCl_2F_2 \rightarrow$ •F + •CCl_2F

C $CCl_2F_2 \rightarrow$ •Cl + •$CClF_2$

D $CCl_2F_2 \rightarrow$ •Cl_2 + •CF_2
Ans: C

Option A shows an impossible reaction as C is the central atom.
Option B shows breaking of C-F bond which is too strong to be broken by UV radiation.
Option C shows breaking of C-Cl bond which is possible to be broken by UV radiation as it is weaker than C-F bond.
Option D is not possible as the 2 Cl are not bonded together in CCl_2F_2.

22 Which hydrocarbons undergo substitution reactions to form only one monochloro-derivative?

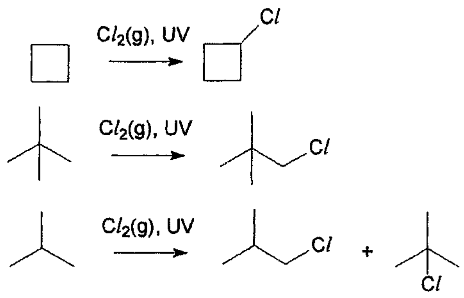
1 cyclobutane

2 2,2-dimethylpropane

3 2-methylpropane

A 1 and 2 only **B** 2 and 3 only **C** 1 and 3 only **D** 1, 2 and 3

Ans: A



23 The alkene 2,4-dimethylpenta-1,3-diene reacts with two moles of HBr to give **X** as the major product.

What is the structure of **X**?

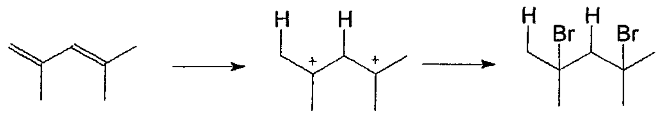
A $CH_2BrCH(CH_3)CH_2CBr(CH_3)_2$

B $CH_2BrCH(CH_3)CHBrCH(CH_3)_2$

C $(CH_3)_2CBrCHBrCH(CH_3)_2$

D $(CH_3)_2CBrCH_2CBr(CH_3)_2$

Ans: D

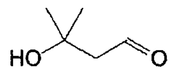


2 tertiary carbocations major product

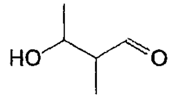
[Turn over

24 Which compound can form an organic product with molecular formula $C_5H_8O_2$ when heated with excess acidified potassium dichromate(VI)?

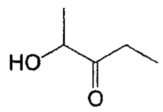
A



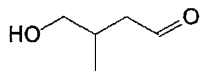
B



C



D

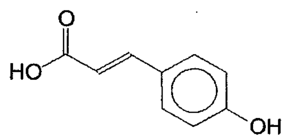


Ans: C

The number of O did not increase, so the compound cannot be any primary alcohols which will become carboxylic acids (increase by 1 O), or aldehydes which will become carboxylic acids (increase by 1 O).

The compound is the one with secondary alcohol(s) which will be oxidised to ketones (no change in number of O)

25 *Para*-coumaric acid is an antioxidant in coffee.



para-coumaric acid

When treated with aqueous bromine, what is the maximum number of bromine atoms that can be incorporated into a molecule of *para*-coumaric acid?

A 2 **B** 3 **C** 4 **D** 5

Ans: C

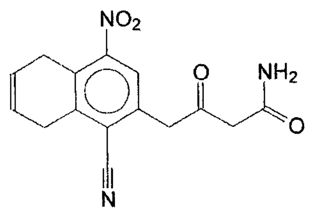
2 Br substituted on 2-position relative to OH

Maximum of 2 Br added across C=C (minor product)

BP-147

BP-148

26



P

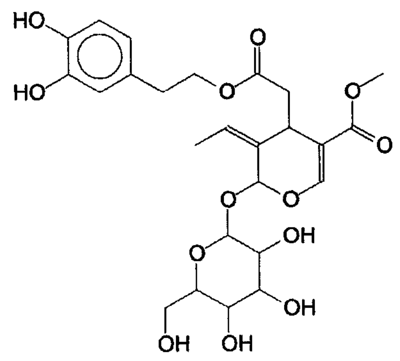
When treated with each of the respective reagents, what is the number of hydrogen atoms that can be incorporated into a molecule of **P**?

	H_2, Ni	$LiAlH_4$ in dry ether	$NaBH_4$ in ethanol
A	6	6	4
B	6	8	4
C	8	6	2
D	8	8	2

Ans: D
H_2,Ni can reduce C=C (+2H), CN (+4H), RCOR (+2H).
$LiAlH_4$ can reduce CN (+4H), RCOR (+2H), $CONH_2$ (+2H).
$NaBH_4$ can reduce RCOR (+2H).

[Turn over

27 Biophenols derived from olives are used as traditional remedies for a variety of conditions, including inflammatory states and cardiovascular diseases. Oleuropein is the most well-known compound of this family and is present in olive tree leaves. Oleuropein has the following structure:



Which statement about oleuropein is correct?

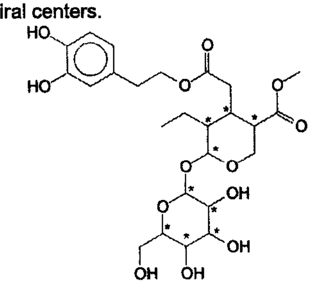
A It does not decolourise cold alkaline $KMnO_4$.

B It reacts with Na_2CO_3 to liberate CO_2 gas.

C A product containing 9 chiral centers is formed when 1 mole of oleuropein reacts with excess H_2 gas in the presence of platinum.

D 6 moles of HC*l* are formed when 1 mole of oleuropein reacts with excess PC*l*$_5$ at room temperature.

Ans: C
Option A is incorrect: Oleuropein contains alkene functional group which can undergo mild oxidation with cold alkaline $KMnO_4$.
Option B is incorrect: Na_2CO_3 reacts with carboxylic acid functional group to liberate CO_2. However, oleuropein does not contain carboxylic acid functional group.
Option C is correct: Alkene functional groups undergo reduction with H_2(g), Pt, to give the following product, with 9 chiral centers.



Option D is incorrect: Nucleophilic substitution of –OH groups in 1 mole of oleuropein to give 4 moles of HC*l*. Phenol does not react with PC*l*$_5$.

28 Methyl ethanoate, CH_3OCOCH_3 undergoes acidic hydrolysis in the presence of $H_2{}^{18}O$.

Which products are formed?

1 $CH_3{}^{18}OH$

2 $CH_3CO^{18}OH$

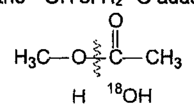
3 CH_3OH

A 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

Ans: C

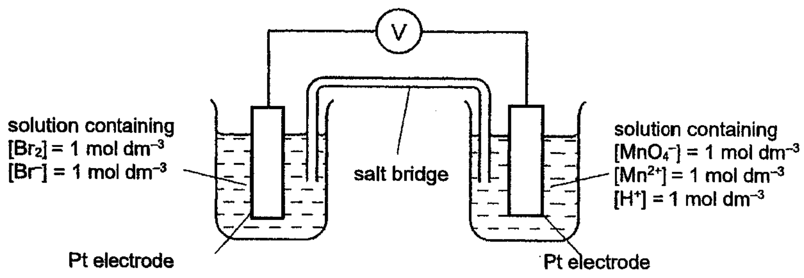
$CH_3OCOCH_3 + H_2{}^{18}O \rightarrow CH_3OH + CH_3CO^{18}OH$

H of $H_2{}^{18}O$ adds to the alcohol and the ^{18}OH of $H_2{}^{18}O$ adds to the carboxylic acid in hydrolysis



29 *Use of the Data Booklet is relevant to this question.*

The following electrochemical cell was set up at 25 °C.



Which of the following statements are true?

1 When silver nitrate crystals are added to the Br_2/Br^- half cell, E_{cell} becomes less positive.

2 The $\Delta G^{\ominus}$ of the above reaction is – 434 kJ mol^{-1}.

3 Addition of water to the MnO_4^-/Mn^{2+} half-cell has no effect on the E_{cell} of the cell.

A 1 only **B** 2 only **C** 1 and 2 only **D** 2 and 3 only

Ans: C

<u>MnO₄</u>$^-$ + 8H$^+$ + 5e ⇌ Mn^{2+} + 4H_2O **(x2)** $E^{\ominus}$ = + 1.52V
Br_2 + 2e ⇌ **2Br$^-$** **(x5)** $E^{\ominus}$ = + 1.07V
Overall equation: **2MnO$_4^-$** + 8H$^+$ + **2Br$^-$** ▯ 2Mn^{2+} + 8H_2O + 5Br_2
$E^{\ominus}_{cell}$ = +1.52 1.07 = +0.45V

Option 1: **True;**
When silver nitrate crystals are added to the Br_2/Br^- half cell,
Ag^+ reacts with Br^-
Br_2 + 2e ⇌ 2Br^-
[Br^-] decreases, POE shifts right and E_{anode} is more positive. Hence E_{cell} becomes less positive.

Option 2: **True;**
$\Delta G^{\ominus} = -nFE^{\ominus}$, where n = 10 electrons transferred
$\Delta G^{\ominus}$ = – (10) x 96500 x (+0.45)
= – 434 kJ mol^{-1} (3 s.f.)

Option 3: False;
Addition of water to the $MnO_4^-/Mn^{2+}/H^+$ will decrease the concentration of all the ions. POE shifts (left) to the side with more ions to increase the concentration, $E_{cathode}$ more negative. E_{cell} more negative.

BP-149

30 When crystalline potassium chromate(VI), K_2CrO_4, was dissolved in water, a yellow solution **P** was formed. The addition of dilute sulfuric acid to **P** gave an orange solution **Q**.

When hydrogen sulfide, H_2S, was bubbled through solution **Q**, the solution changed colour and gave a solution **R**, with a yellow solid.

Which process does **not** occur in this sequence?

A Ligand exchange reaction

B Acid-base reaction

C Redox reaction

D Precipitation reaction

Ans: A

Yellow solution **P** is CrO_4^{2-}(aq). When sulfuric acid is added to **P**, acid-base reaction occurs to give orange solution **Q**, $Cr_2O_7^{2-}$.

$$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

When hydrogen sulfide is bubbled into **Q**, redox reaction & precipitation occurs to give solution **R**, Cr^{3+}(aq) and yellow solid, S.

$$3H_2S + Cr_2O_7^{2-} + 8H^+ \rightarrow 3S + 2Cr^{3+} + 7H_2O$$

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS | REGISTRATION NUMBER

CHEMISTRY

9729/02

Paper 2 Structured Questions

16 September 2025
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use paper clips, highlighters, glue or correction fluid.

Answers **all** questions.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/16
2	/14
3	/17
4	/16
5	/12
Paper 2 Total	/75

	Marks	Weightings
Paper 1	/30	15%
Paper 2	/75	30%
Paper 3	/80	35%
Paper 4	/55	20%

Overall Percentag e	
Grade	

This document consists of **19** printed pages and **1** blank page.

[Turn over

Answer **all** the questions in the spaces provided.

1 925 silver, also known as sterling silver, is an alloy that is commonly used to make jewellery. It consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $Ag_2S(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.

$$2Ag(s) + H_2S(g) \downarrow\square\ Ag_2S(s) + H_2(g)$$

(a) (i) Write the full electronic configuration for copper.
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Note: Cu has a special configuration of $3d^{10}\ 4s^1$
Common mistakes
- Putting $4s^1$ before $3d^{10}$
- Configuration written as $1s_2\ 2s_2\ 2p_6\ 3s_2\ 3p_6\ 3d_{10}\ 4s_1$

[1]

(ii) State and explain the difference in atomic radii for silver and copper.
Ag has one more filled electronic shell than Cu. The **distance of its valence electron is further away from nucleus and experience higher shielding effect**. This **outweighs the higher nuclear charge in Ag**. **Nuclear attraction for the outermost electron** in Ag is **weaker**. Thus, **atomic radius of Ag is larger**.
Common mistakes
- Students mention shielding effect but **did not state the further distance as a factor as well.**
- Another common mistake is that having more electrons/more inner subshells does not always means a further distance of the valence electrons from the nucleus.
- Students mention both nuclear charge and shielding effect being higher for Ag but did not mention that the higher shielding effect and further distance **outweighs** the higher nuclear charge.
- Students also often miss out nuclear attraction for the **valence electrons.**
- Outweigh and **not** offset/nullified/cancelled out.

[2]

(b) The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the Ag_2S and records the data in Table 1.1.

Table 1.1

mass before Tarnish Removal /g	54.23
mass after Tarnish Removal /g	52.34

BP-151

BP-152

Assuming that only Ag_2S (s) is removed, calculate the number of moles of silver atoms removed.
Mass of Ag_2S removed = 54.23 – 52.34 = 1.89 g.

Amount of Ag_2S removed = $\frac{1.89}{2(107.9)+32.1} = \frac{1.89}{247.9}$
= 0.00762 mol

$2Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$

Amount of Ag removed = 2 × 0.00762
= **0.0152 mol**

Common mistakes

- Students did not use the mole ratio to find the number of mol of Ag removed
- Many students calculated the no of atom instead of no of mole of Ag

[1]

(c) (i) Suggest and explain the relative magnitude of the lattice energy of the silver compounds Ag_2S, Ag_2O and Ag_2Se.

$|L.E| \propto |\frac{q_+ \times q_-}{r_+ + r_-}|$ circle but don't penalize if put "="

- **Product of charges ($q_+ \times q_-$) and the cationic radius (r_+) for Ag_2O, Ag_2S, Ag_2Se are the same**
- **Interionic distance of $Ag_2O < Ag_2S < Ag_2Se$ OR Anion radius of $O^{2-} < S^{2-} < Se^{2-}$**
- Since $|L.E| \propto |\frac{q_+ \times q_-}{r_+ + r_-}|$, **magnitude of lattice energy of $Ag_2O > Ag_2S > Ag_2Se$**

Common mistakes

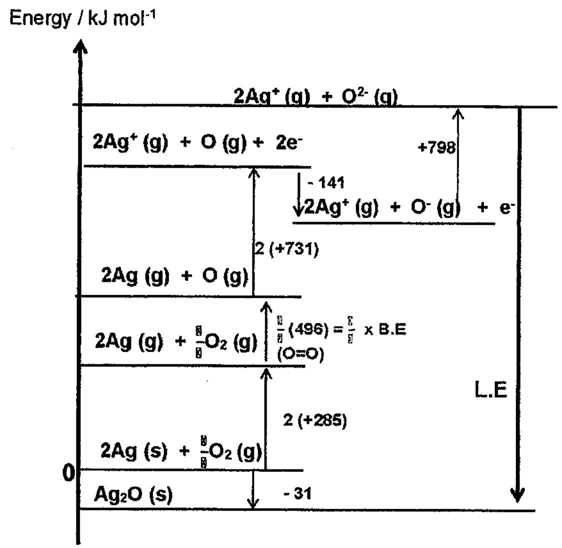
- Students did not state the $|L.E| \propto |\frac{q_+ \times q_-}{r_+ + r_-}|$ in the answer
- Students mention atomic radius comparison rather than the ionic radius.

[2]

(ii) Using relevant data from the *Data Booklet* and Table 1.2, calculate the lattice energy of Ag_2O.

Table 1.2

standard enthalpy change of atomisation of silver	+285 kJ mol^{-1}
1st electron affinity of oxygen	–141 kJ mol^{-1}
2nd electron affinity of oxygen	+798 kJ mol^{-1}
standard enthalpy change of formation of $Ag_2O(s)$	–31 kJ mol^{-1}



By Hess Law,

$-31 = 2(285) + \frac{1}{2}(496) + 2(731) + (-141) + 798 + L.E$

L.E = -2968 = <u>-2970 kJ mol^{-1}</u>

<u>Common mistakes</u>

- Axis not drawn
- Putting Electron affinity before Ionisation energy in the energy level diagram
- Bond energy for the oxygen is left out.
- Students forget to x2 to the ionisation energy of Ag but instead include in 2nd I.E for Ag
- Students are not familiar with the use of Hess's law. Many students changed the ΔH_f sign for $Ag_2O(s)$ to +31kJmol^{-1} and 1st EA of O to +141kJmol^{-1}.

[4]

(d) Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, Rh(s), onto the surface of the metal from an acidified solution of $Rh_2(SO_4)_3$ (aq). Oxygen gas is produced during this process.

One of the half equations involved in this reaction is

$Rh^{3+} + 3e \rightleftharpoons Rh$ $\qquad$ $E^\circ = +0.76$ V

(i) Write the half equation for the reaction that has resulted in the formation of oxygen gas in this reaction and hence, write the balanced ionic equation for the overall reaction.

[O] : $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

cannot accept reversible arrow.

$4Rh^{3+}$ (aq) + $6H_2O$ (*l*) ↓□ 4Rh (s) + $3O_2$ (g) + $12H^+$ (*aq*)

must have state symbol for ionic equation

<u>Common mistakes</u>

- **[O]** equation not written with □
- The basic equation is chosen instead.
- The balanced equation does not have state symbol

[2]

(ii) Calculate the value of E°_{cell} for the overall reaction in part **(i)**.

$E^\circ_{cell} = E^\circ_{Red} - E^\circ_{ox}$

$= +0.76\text{ V} - 1.23\text{ V}$

= **<u>−0.47 V</u>**

[1]

(iii) Based on your answer to part **(ii)**, explain why this process requires the use of an external power source.

E°_{cell} **<u>is negative,</u>** which means the reaction is **<u>not energetically feasible</u>** and thus **<u>energy must be supplied for the reaction to occur</u>**.

Generally, well done

[1]

(iv) Calculate the current that must be supplied for 3.5 g of Rh to be plated onto a piece of sterling silver in 3 minutes.

At the cathode: **[R] $Rh^{3+} + 3e^- \longrightarrow Rh$**

Amount of Rh deposited = $\frac{3.5}{102.9}$ = 0.0340 mol

$\eta_e = 3 \times 0.0340 = 0.102$ mol

$I \times t = \eta_e \times F$

$I = \frac{n_e \times F}{t} = \frac{0.102 \times 96500}{3 \times 60}$ = **<u>54.7A</u>**

Generally, well done

[2]

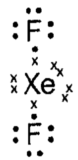
[Total : 16]

BP-153

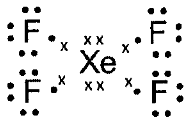
BP-154

2 (a) Xenon is a noble gas and forms various fluorides with fluorine. Two of these are xenon difluoride, XeF_2, and xenon tetrafluoride, XeF_4, which are crystalline solids with melting points of 140 °C and 112 °C respectively.

(i) Draw the dot-and-cross diagrams for XeF_2 and XeF_4 and hence state their molecular shapes.



XeF_2: linear



XeF_4: square planar

[3]

Common mistakes

- Students missed out drawing the 3 lone pair electrons on F atom.
- Students are still unsure of the molecular shapes associated with the different number of lone pairs & bond pairs.

(ii) Even though XeF_4 has more electrons and is hence expected to have greater intermolecular forces than XeF_2, its melting point is lower. Suggest why XeF_2 has a higher melting point than XeF_4.
There is higher packing efficiency in the linear XeF_2 molecules compared to the square planar XeF_4 molecules, thus intermolecular forces are stronger between XeF_2 molecules, requiring more energy to overcome, hence higher melting point.

[1]

Common mistakes

- Students incorrectly identified XeF_2 as a polar molecule and explained that the pd-pd interactions are stronger than id-id between the non-polar XeF_4.

(iii) Using your knowledge of covalent bond formation, explain why
- Xenon reacts with fluorine but neon does not
- Xenon reacts with fluorine but not with iodine

Xenon is in Period 5, hence able to expand octet due to availability of vacant energetically accessible orbitals (empty low-lying orbitals) to accommodate additional electrons from fluorine during covalent bond formation but neon is unable to expand octet as it is in Period 2.

Common mistakes

- Common misconception is that neon already has a full octet structure hence does not undergo reaction with other elements while xenon has not fulfilled octet structure yet.

Fluorine has smaller atomic radius than iodine, Xe-F bond hence has shorter bond length and is stronger than Xe-I bond

Common mistakes

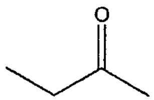
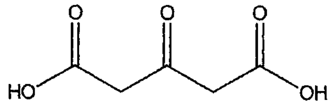
- Many students explained that since fluorine is more electronegative than iodine, hence it can better attract the electrons from xenon towards itself, forming a stronger bond.
- Do note that when we compare covalent bond strength, we look at the following factors:
  1. Bond order (strength of triple bond > double bond > single bond)
  2. Effectiveness of orbital overlap (smaller orbitals are less diffused, hence generally have more effective orbital overlap resulting in a stronger bond)
  3. Bond Polarity (this factor is used only when comparing 2 bonds with similar bond order, similar effectiveness of orbital overlap, eg comparing between C-C and C-F bond. C-F bond is stronger due to difference in electronegativity between C & F)

[2]

(b) **P** and **Q** are compounds containing the same functional groups.

Both compounds
- readily decolourise bromine in the dark
- liberate a gas with sodium metal
- do not have O atom bonded to an unsaturated carbon atom
- react with hot acidified potassium manganate(VII) to give the products as shown in Table 2.1.

Table 2.1

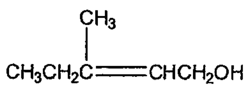
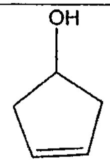
compound	products of oxidation
P ($C_6H_{12}O$)	 and CO_2
Q (C_5H_8O)	

(i) Considering the molecular formulae of the two compounds together with the information given above, name the two functional groups that are present in compounds **P** and **Q**.
Alkene and alcohol

[2]

Generally well done

(ii) Suggest the structures of compounds **P** and **Q**.

Compound **P**	Compound **Q**
	

Note: For compound **P**, $=CHCH_2OH$ oxidises to give ethanedioic acid, HOOC-COOH, which is further oxidized by $KMnO_4$ to give $2CO_2 + H_2O$

Note: From Table 2.1 , oxidation of **Q** gives only one product with same number of carbon atoms as **Q**, we can deduce that **Q** contains C=C in a cyclic ring.

[2]

Common mistakes

- Students incorrectly drew terminal alkene for **P** without realising that although terminal alkenes can give rise to CO_2 product, it will also give a carboxylic acid product, which does not tally with the products given in Table 2.1.

BP-155

BP~156

(c) Compound **R**, $C_9H_{18}O_2$, has the same two functional groups as **P** and **Q** in **(b)**. Upon strong oxidation by hot acidified $KMnO_4$, compound **S**, $C_6H_{12}O_2$, and compound **T**, $C_3H_4O_3$, are obtained.

The following four reagents were used to test compounds **S** and **T** and the results are shown in the table below.

test reagent	result of test with	
	compound **S**	compound **T**
Na(s)	fizzes	fizzes
$NaHCO_3$(aq)	no reaction	fizzes
I_2(aq) + OH (aq), warm	no reaction	yellow ppt
2,4-DNPH	orange ppt	orange ppt

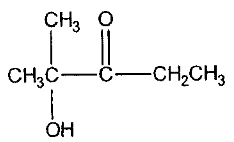
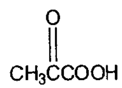
(i) By considering the test results with Na(s) and $NaHCO_3$(aq), name the functional group that is present in **S** and **T**.

Functional group present in **S**: Alcohol

Functional group present in **T**: Carboxylic acid [2]

Generally well done

(ii) Suggest the structures of compounds **S** and **T**.

Compound **S**	Compound **T**
	

Note: **S** must contain a tertiary alcohol (remains unaffected by oxidation of **R** with hot acidified $KMnO_4$). **S** cannot have $-COCH_3$ group as it does not give yellow ppt with warm alkaline I_2.

[2]

Common mistakes

- Many incorrect structures for **S** were drawn, including those having aldehyde (which should not be present since **R** was oxidised by strong oxidising agent $KMnO_4$

[Total : 14]

[Turn over

3 (a) A sodium ethoxide slurry is prepared by dissolving sodium in dry ethanol. When this slurry is transferred into liquid dimethyl ether, CH_3OCH_3, at 40 °C, the following equilibrium is established.

$$CH_3CH_2ONa + 6CH_3OCH_3 \rightleftharpoons [Na(CH_3OCH_3)_6]^+ + CH_3CH_2O^-$$

(i) Write a balanced equation for the reaction of ethanol with sodium.
$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2$

[1]

Common mistakes

1. Writing H^+ as product.
2. Mistaking ethanol (CH_3CH_2OH) as CH_3COOH

(ii) Using your knowledge of VSEPR theory, state and explain the bond angle around the oxygen atom in CH_3OCH_3.
For CH_3OCH_3, there are **2 bond pairs and 2 lone pairs of electrons** around the O atom.

By VSEPR theory, electron regions around the central O atom are spread out to minimise mutual repulsion. Since **lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion**, the bond angle is **105° or (104.5°)**

Common mistakes

1. Not stating clearly the order of lone pair-lone pair, lone pair-bond pair and bond pair-bond pair repulsions.
2. Not mentioning the idea that electron regions are "spread out" or "arranged as far as possible" to "minimise repulsion".

[2]

(b) The strongly basic ethoxide ion, CH_3CH_2O then removes a proton from compound **A**, giving the anion shown in Fig. 3.1.

Intramolecular attack of the anion on the C–C*l* bond forms compound **B**.

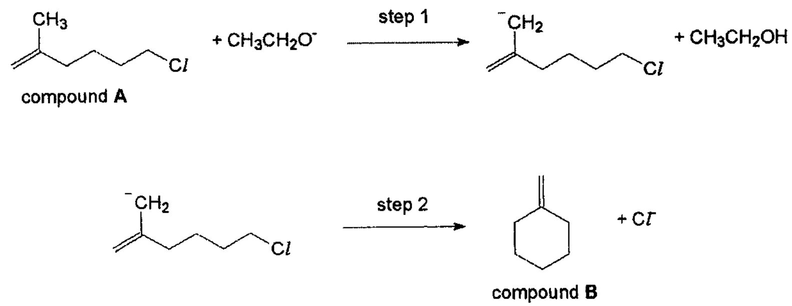
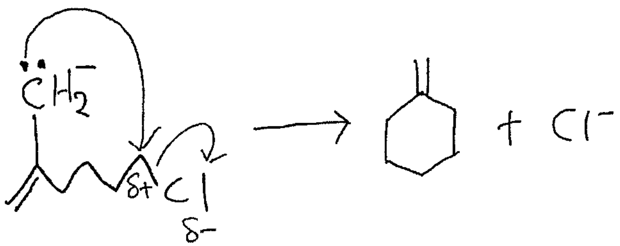


Fig. 3.1

Show the mechanism for step 2 on Fig. 3.1 by adding a lone pair, curly arrows and dipoles.

State the name of the mechanism involved.

Nucleophilic substitution



This was generally well done. Common mistake is to forget to draw the lone pair on the carbon atom of the $–CH_2^-$ group.

[2]

(c) **Finely powdered sodium ethoxide burns in excess oxygen to give sodium carbonate, carbon dioxide and water as the only products.**

Balance the chemical equation for this combustion.

……CH_3CH_2ONa + ……O_2 → Na_2CO_3 + …..CO_2 + ……H_2O
$2CH_3CH_2ONa + 6O_2 \rightarrow Na_2CO_3 + 3CO_2 + 5H_2O$

Many students found it difficult to balance this equation.

[1]

(d) **Given the pK_a values, explain the order of acidity of the following compounds in aqueous medium.**

compound	pK_a
ethanol	15.9
phenol	10.0
ethanoic acid	4.76

$CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$
$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$
$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

The electron-donating alkyl group (CH_3CH_2-) destabilize $CH_3CH_2O^-$ by intensifying its negative charge. The negative charge of $C_6H_5O^-$ is dispersed into the benzene ring via resonance. The negative charge of CH_3COO^- is dispersed **significantly** over 2 highly electronegative O atoms via resonance.

Stability of CH_3COO^- > $C_6H_5O^-$ > $CH_3CH_2O^-$

Ethanoic acid dissociates most readily into H^+ and its conjugate base, followed by phenol and lastly ethanol. Hence acidity of ethanoic acid > phenol > alcohol.

This question was not well done.

Common mistakes

1. Referring to the acid molecules when talking about "dispersal of negative charges" and the "intensification of negative charge" or when talking about "stability". Students should be referring to their respective conjugate bases instead.

Many students are ambiguously using the name of the acid and its conjugate base interchangeably as if they are referring to the same thing. Also, many are using the pronoun "it" in an ambiguous manner to refer to the acid and its conjugate base in the same sentence. This makes it hard for the marker to award marks.

2. Focusing on "delocalization of the lone pair electrons on O atom" in the phenol and ethanoic acid molecules, rather than to focus on the "dispersal of negative charge" in the phenoxide and ethanoate ions.

3. Not clearly stating the orders of "stability of conjugate bases" and the "extent of dissociation of the acid molecules".

4. A number of students used incorrect terms to refer to the conjugate base of ethanol and do not seem to know that the conjugate base of ethanol is called "ethoxide", despite the name of the salt "sodium ethoxide" being used in the question stems in 3(a) and 3(c).

[3]

BP-157

BP-158

(e) 2-bromobutane can be used to synthesise propanoic acid by the three-step route shown in Fig. 3.2.

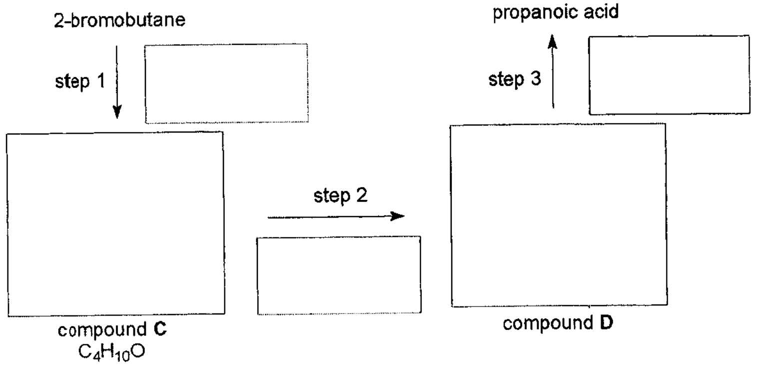
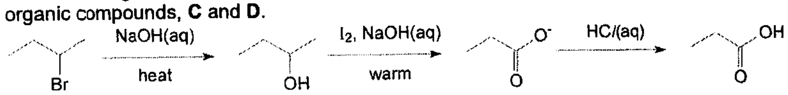
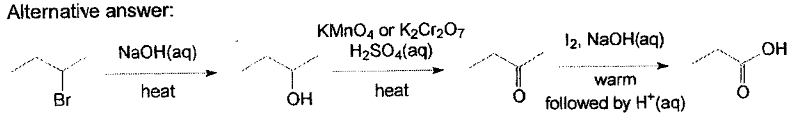


Fig. 3.2

State the reagents and conditions required for each step and suggest structures for the organic compounds, **C** and **D**.



Alternative answer:



Common mistakes

1. Using ethanolic NaOH to convert 2-bromobutane to butan-2-ol.
2. Forgetting to write (aq) when referring to NaOH (aq). It is important to write the (aq) for step 1 since there is a difference between using aqueous NaOH and ethanolic NaOH.
3. Writing "acidified $KMnO_4$" instead of writing "H_2SO_4(aq) and $KMnO_4$".

[5]

(d) **The K_b of a secondary amine, $R_1(R_2)NH$, is 5.75×10^{-4} mol dm^{-3}. A 1.50 g sample of the amine is dissolved in water and the solution is made up to 1.00 dm^3. The pH of the resulting solution is 11.55.**

Calculate the relative molecular mass of $R_1(R_2)NH$, and suggest a structural formula for $R_1(R_2)NH$. Show your working clearly.

Amount of $R_1(R_2)NH = \frac{1.50}{M_r}$ mol

Initial $[R_1(R_2)NH] = \frac{1.50}{M_r}$ mol dm^{-3}

For weak base,

$[OH^-] = \sqrt{K_b \times [R_1(R_2)NH]}$

Given pH = 11.55, pOH = 14 – 11.62 = 2.45

$[OH^-] = 10^{-2.45}$ mol dm^{-3}

$[R_1(R_2)NH] = \frac{[OH^-]^2}{K_b} = \frac{(10^{-2.45})^2}{5.75\times10^{-4}} = 0.02189$ mol dm^{-3}

$\frac{1.50}{M_r} = 0.02189$

$M_r = 68.5$

The secondary amine is $CH_2=CH(CH_2=CH)NH$ ($M_r = 69$).

Alternative method:

$R_1(R_2)NH + H_2O \rightleftharpoons R_1(R_2)NH_2^+ + OH^-$

$[OH^-]_{eqm} = 10^{-2.45} = 0.003548$ mol dm^{-3} $= [R_1(R_2)NH_2^+]_{eqm}$

$[R_1(R_2)NH]_{eqm} = \frac{1.50}{M_r} - 0.003548$

$$K_b = \frac{[R_1(R_2)NH_2^+]_{eqm}[OH^-]_{eqm}}{[R_1(R_2)NH]_{eqm}}$$

$$5.75 \times 10^{-4} = \frac{(0.003548)(0.003548)}{\frac{1.50}{M_r} - 0.003548}$$

$\frac{1.50}{M_r} - 0.003548 = 0.02189$

$\frac{1.50}{M_r} = 0.02544$

$M_r = 58.9$

The secondary amine is $CH_3CH_2(CH_3)NH$ ($M_r = 59$).

Many students were able to calculate the Mr of the secondary amine, but few were able to give the correct structural formula of the amine.
A common mistake is to write the unit g mol^{-1} or even g for the Mr calculated.

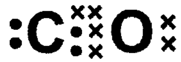
[3]

[Total : 17]

[Turn over

4 Although carbon monoxide, CO, is a poisonous gas, it is an important starting material in the synthesis of many industrially important compounds.

(a) **(i)** Draw a 'dot–and–cross' diagram to show the bonding in carbon monoxide.



Common mistakes

- The dot and cross drawn shows Oxygen having more than 8 electrons in the outermost shell.

[1]

(ii) Suggest why carbon monoxide is poisonous.
Carbon monoxide **binds more strongly than O_2** with iron ion in haemoglobin to form **very stable complexes**. This **cuts down the supply of oxygen to the body**.
Common mistakes

- Students did not give the idea that carbon monoxide forms a more stable complex relative to oxygen/the more stable complex with CO ligand unlikely to be replaced by the oxygen.

[1]

Carbon monoxide can undergo water–gas shift reaction. The carbon monoxide gas reacts with steam to produce carbon dioxide gas and hydrogen gas.

reaction 4.1 $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

(b) Explain the difference in boiling points of CO and of CO_2 in terms of the type and relative strength of the intermolecular forces.

species	boiling point/ °C
CO	–191
CO_2	–78

Both CO and CO_2 have simple molecular structure, with **permanent dipole–permanent dipole (pd–pd) interaction and instantaneous dipole–induced dipole (id–id) interaction between the CO molecules** and **id–id interaction between the CO_2 molecules** CO_2 has a higher M_r and a **larger electron cloud than CO, dipole is more easily induced** resulting in **stronger id–id interactions**. More energy is required to overcome the stronger id–id interactions between CO_2 molecules than the intermolecular forces of attraction between CO molecules. Therefore, CO_2 has a higher boiling point than CO.
Common mistakes

- Students mistaken identify both CO and CO_2 being polar and compare the difference due to pd-pd
- Students did not identify the presence of id-id between CO on top of the pd-pd.

[2]

BP~159

BP-160

(c) 0.200 mol of carbon monoxide and 0.200 mol of steam was placed in reaction vessel and allowed to react at a temperature of 800 K. The percentage of carbon monoxide reacted was found to be 77.5%.

reaction 4.1 $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

(i) Write the expression for the equilibrium constant, K_c, for reaction 4.1.

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

Common mistakes

- Students ignore the $[H_20]$ in the expression. It should be included as it is homogenous system. The states of all the species are gas.

[1]

(ii) Calculate the value of the equilibrium constant, K_c, at 800 K.

	CO(g)	+	$H_2O(g)$	⇌	$CO_2(g)$	+	$H_2(g)$
Initial / mol	0.200		0.200		0		0
change / mol	−0.2×0.775		−0.2×0.775		+0.2×0.775		+0.2×0.775
Eqm / mol	0.045		0.045		0.155		0.155

$$K_c = \frac{\left(\frac{0.155}{V}\right)\left(\frac{0.155}{V}\right)}{\left(\frac{0.045}{V}\right)\left(\frac{0.045}{V}\right)} = 11.86 \approx 11.9$$

Common mistakes

- Students tried to calculate the pressure of each species to calculate the K_c.

[2]

(iii) The Gibbs free energy change of reaction, ΔG_r, for reaction 4.1 is −18.4 kJ mol^{-1} at 600 K. The relationship between the equilibrium constant and the Gibbs free energy change of this reaction can be expressed as:

$$\Delta G = -RT \ln K_c$$

Calculate the value of K_c for the reaction 4.1 at 600 K.

$-18.4 \times 10^3 = -(8.31)(600) \ln K_c$

$\ln K_c = 3.690$

$K_c = 40.04 \approx 40.0$

Note: need to convert ⊗G to J mol^{-1}

[1]

[Turn over

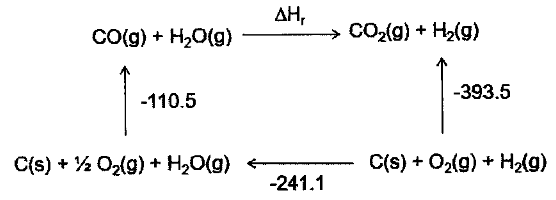
(d) Table 4.1 gives data relevant to this question.

Table 4.1

$\otimes H_f^{\circ}$ CO(g)	−110.5 kJ mol^{-1}
$\otimes H_f^{\circ}$ $CO_2(g)$	−393.5 kJ mol^{-1}
$\otimes H_f^{\circ}$ $H_2O(g)$	−241.1 kJ mol^{-1}

Using the data given in Table 4.1, construct an energy cycle to calculate the enthalpy change of reaction for reaction 4.1.

reaction 4.1 $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$



Ok to combine $\otimes H_f^{o}(CO) + \otimes H_f^{o}(H_2O)$

By Hess' Law,

ΔH_r = − (−110.5) − (−241.1) + (−393.5)

= **−41.9 kJ mol^{-1}**

Most students were able to draw the Hess cycle and calculate the answer correctly. Most common mistakes in the Hess Cycle are to copy the reversible arrow into the Hess Cycle from the question and to omit state symbols in some parts of the cycle.

[2]

(e) The English chemist William Henry studied the equilibria when an ideal gas dissolves in a liquid. He proposed that the concentration of the gas dissolved in a liquid is proportional to the partial pressure of the gas above the liquid surface. This proportionality factor is called Henry's law constant, K_H. The Henry's law constant, K_H can be represented as the equation below.

$$K_H = \frac{maximum\ concentration\ of\ gas\ dissolved\ in\ mol\ dm^3}{partial\ pressure\ of\ gas\ in\ atm}$$

Sealed containers of fizzy drinks contain dissolved CO_2. This dissolved CO_2 is in equilibrium with a very small quantity of gaseous CO_2 at the top of the container.

reaction 4.2 $CO_2\,(g) \rightleftharpoons CO_2\,(aq)$

The Henry's law constant for CO_2 is 3.3×10^{-2} mol dm^{-3} atm^{-1} at 25 °C.

(i) The partial pressure of CO_2 gas in a can of 250 cm^3 fizzy drink is 3.0 atm at 25 °C.

Calculate the concentration of CO_2 in the fizzy drink and hence the mass of CO_2 dissolved in the 250 cm^3 of fizzy drink.

$$K_H = \frac{maximum\ concentration\ of\ gas\ dissolved\ in\ mol\ dm^{-3}}{partial\ pressure\ of\ gas\ in\ atm}$$

$$3.3 \times 10^{-2} = \frac{maximum\ concentration\ of\ gas\ dissolved\ in\ mol\ dm^{-3}}{3}$$

$[CO_2]$ = 0.0990 mol dm ^{3}

Amount of $CO_2 = 0.0990 \times \frac{250}{1000} = 0.02475$ mol

Mass of CO_2 = 0.02475 × (12 + 16 + 16)
= 1.089
= 1.09 g (3s.f.)

This question was well done by most. A small number of students forgot to write the unit for the concentration of CO_2.

[2]

(ii) The maximum pressure that a can of fizzy drink can withstand is 6.2 atm. Using Fig. 4.1, determine the maximum temperature at which the fizzy drink can can be stored safely.

You may assume that the maximum amount of CO_2 that is dissolved remains the same.

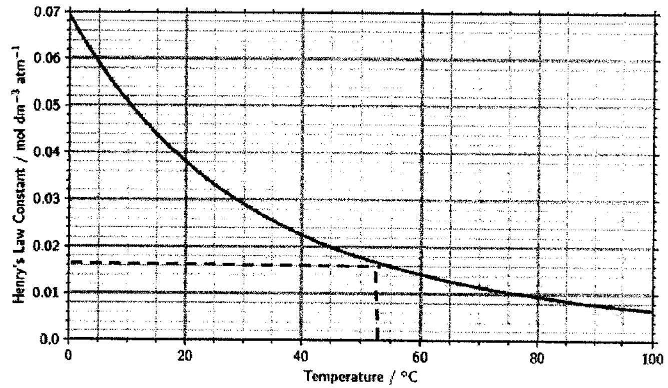


Fig. 4.1

***Note :** In a sealed container, the gas is essentially trapped within the liquid and the small amount of space above, leading to minimal gas particles in that space. So when the pressure is increased, the change in the concentration in the liquid will be minimal*

$K_H = \frac{0.099}{6.2}$
= 0.0160 mol dm^{-3} atm^{-1}

From the graph,
Maximum temp = <u>**52°C – 55°C**</u>

This question was well done by most.

[2]

(iii) Hence, deduce with reasoning, the sign of enthalpy change for reaction 4.2.
When the **temperature is increased**, by *Le Chatelier's* Principle, the system will **partially decrease** the temperature **by absorbing heat.** The position of equilibrium will **shift to favour endothermic reaction.**

As seen from graph, when **temperature is increased**, the **Henry's law constant, K_H decreased**, the position of equilibrium has **shift left to favour endothermic reaction.**

Hence forward reaction is exothermic and the enthalpy change is negative.

Not so well done. Answers that simply stated the enthalpy change as negative without explicitly referring to the forward reaction as being exothermic were not given any credit.

BP-161

Some students who gave the correct explanation forgot to mention the sign of the enthalpy change.

[2]

[Total : 16]

[Turn over

5 **Plastic takeaway containers for food are commonly made of polypropene (PP) which is microwave safe and chemically inert.**

Polymerisation is a chemical process where small molecules (monomers) combine to form a large molecule (polymer) through the formation of covalent bonds. Fig 5.1 shows the process of joining many propene monomers to form polypropene. The type of polymerisation is known as addition polymerisation as only 1 single product is formed.

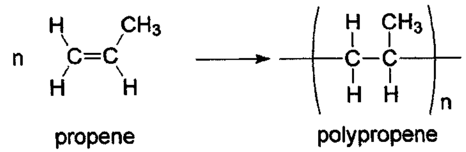


Fig 5.1

(a) (i) **The polymerisation of 1 mole of propene to form polypropene (Fig 5.1) has a standard entropy change of -110 J mol^{-1} K^{-1}.**

Account for the negative sign of the standard entropy change for polymerisation.
Amount of **gaseous** particles decreases from 1 mole to 0 (polypropene is a solid), resulting in **less ways to arrange the particles and their energies**.

[2]

Common mistakes

- Students merely mentioned that there is a decrease in number of particles during polymerisation.
- Recap the factors that we use to explain changes in entropy:
  1. Change in the number of gaseous particles
  2. Mixing of particles (no chemical reaction)
  3. Change in phase (physical change)
  4. Change in temperature

(ii) **Given that the standard enthalpy change of polymerisation of polypropene is -55.0 kJ mol^{-1}, calculate the maximum temperature for the reaction to be spontaneous.**

$\Delta G = \Delta H - T\Delta S < 0$
$-55 - T(-110 \times 10^{-3}) < 0$
$T < 500$ K

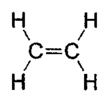
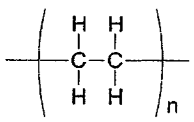
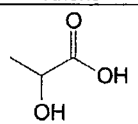
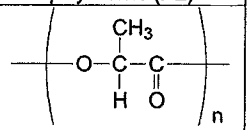
Maximum T is 499 K

Common mistakes

- Many students leave their answer as 500 K without realising that they should suggest a maximum temperature that is less than 500 K.

[2]

The increasing environmental concerns over plastic pollution have led to innovations in food packaging design. Many food establishments now use paper-based takeaway containers coated with either polyethene (PE) or polylactic acid (PLA) instead of conventional plastic containers.

monomer	polymer
 ethene	 polyethene (PE)
 lactic acid	 polylactic acid (PLA)

(b) **(i)** State the IUPAC name of lactic acid.
2-hydroxypropanoic acid

[1]

Common mistakes
- Some students put a hyphen between the hydroxy and propanoic acid
- Some students wrote 'hydroxyl' instead. Note that hydroxyl refers to the alcohol functional group.

(ii) Similar to propene, ethene undergoes addition polymerisation to form polyethene. Lactic acid undergoes a different type of polymerisation as a by-product is formed. Identify the by-product and hence state the type of polymerisation undergone by lactic acid to form PLA.

By-product: H_2O

Type of polymerisation: Condensation polymerisation

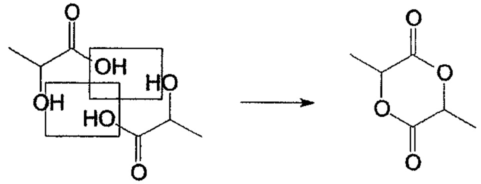
[1]

(iii) The equation for polymerisation of lactic acid to form PLA is found to be:

$$2n\ CH_3CH(OH)CO_2H \rightarrow n\ \mathbf{X} + \text{by-product} \rightarrow PLA$$

X is a cyclic intermediate with the molecular formula of $C_6H_8O_4$.
X does not react with Na.

Draw the skeletal structure of **X**.



X

[1]

(c) Tom Yum soup is cooked with Thai bird's eye chilies, lime juice and lemongrass to give the characteristic sour and spicy flavour. A Thai food stall vendor is choosing between takeaway food containers coated with PE or PLA to contain hot Tom Yum soup.

By considering the structures of PE and PLA, and the properties of Tom Yum soup, explain which type of takeaway food container you would recommend to the Thai food stall vendor.

I would recommend PE

As Tom Yum soup is acidic and hot, the ester bond in PLA is likely to undergo acidic hydrolysis.

PE will not undergo acidic hydrolysis.

[2]

Common mistakes
- Some students explained that PLA has pd-pd interactions between polymers, requiring more energy to overcome compared to id-id between PE, hence have higher melting point and can withstand hot food.

BP-163

(d) Microplastics are particles with sizes ranging from 1 μm to 5 mm in any dimension (1 mm = 1000 μm).

While PE-coated and PLA-coated paper containers still contain plastic elements, they use significantly less plastic than traditional PP containers, thereby reducing the potential for microplastic generation.

A researcher studied the degradation of samples of PE and PLA in an aqueous condition with a similar salt concentration as seawater and with exposure to UV light after 2 years. He then determined the proportion of particles with various sizes of ≤3 μm, as shown in Fig 5.2.

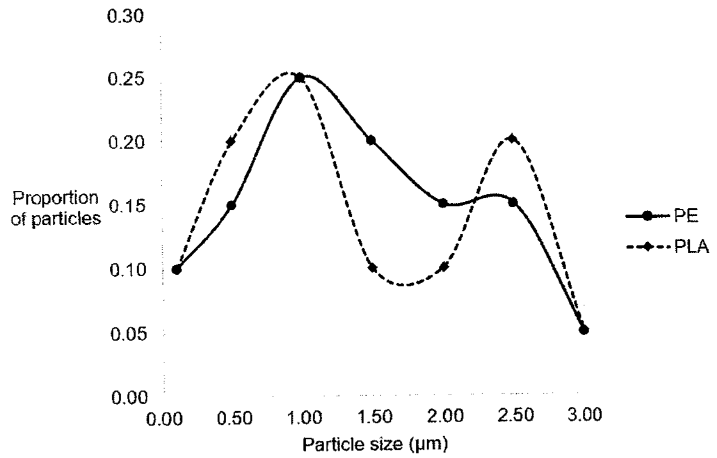


Fig 5.2

(i) With reference to Fig 5.2, explain whether you would expect PE or PLA to degrade and generate more microplastics in the sea.
There is a greater proportion of particles (0.25+0.2+0.15+0.15+0.05=0.80) of particle size greater than from 1 μm to 3 mm from PE than from PLA (0.25+0.10+0.10+0.2+0.05 =0.70)

Therefore, PE generates more microplastics in the sea.

or

PE generates more microplastics in the sea.
Area under the graph of PE is greater than PLA for sizes from 1 μm to 3 mm.

[2]

(ii) State one other condition for the degradation of PE and PLA in the sea that the researcher should have considered in his investigation.

Acceptable answers include:
Temperature of seawater
pH of seawater
Wave action
Pressure of seawater

Note that answers given must be related to conditions of the sea

[1]

[Total: 12]

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS | REGISTRATION NUMBER

CHEMISTRY **9729/03**
Paper 3 Free Response
23 September 2025
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Section A	
1	/19
2	/20
3	/21
Section B (*circle the question you attempted)	
4	/20
5	/20
Paper 3 Total	/80

This document consists of **28** printed pages.

[Turn over

Section A

Answer **all** the questions in this section.

1 (a) A student investigated the thermal decomposition of Group 2 compounds. He heated a mixture of 2.50 g of magnesium nitrate and magnesium carbonate using the setup shown in Fig. 1.1, till no further change was observed. A colourless gas of a volume of 80.8 cm^3 was collected at 30 °C and atmospheric pressure.

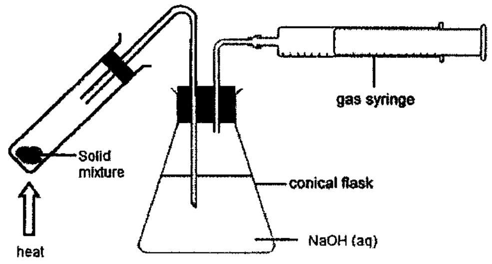


Fig 1.1

(i) Write balanced equations for the thermal decomposition of $MgCO_3$ and $Mg(NO_3)_2$. [1]

$MgCO_3$ □ $MgO + CO_2$
$Mg(NO_3)_2$ □ $MgO + 2\ NO_2 + ½\ O_2$

(ii) Explain the purpose of sodium hydroxide in the above setup and hence identify the gas collected in the gas syringe. [2]
NaOH(aq) reacts with the acidic gases (CO_2 and NO_2).

The gas collected in the gas syringe is O_2.

(iii) Calculate the percentage by mass of magnesium nitrate present in the mixture. [3]
$Mg(NO_3)_2$ □ $MgO + 2\ NO_2 + ½\ O_2$

pV = nRT

Amount of O_2 gas collected = $\frac{101325 \times 80.8 \times 10^{-6}}{8.31 \times (30+273)}$ = 0.003252 mol
Amount of $Mg(NO_3)_2$ = 2 · 0.003252 = 0.006504 mol
Mass of $Mg(NO_3)_2$ = 0.006504 · (24.3+14·2+16·6) = 0.9644 g
% by mass of $Mg(NO_3)_2$ in mixture = $\frac{0.9644}{2.50}$ · 100% = 38.6 %

BP-165

BP-166

(b) The student carried out another experiment by heating equal amounts of carbonates of magnesium, calcium and barium for two minutes using a Bunsen burner. Table 1.1 shows the volume of gas collected.

Table 1.1

Group 2 carbonate	$MgCO_3$	$CaCO_3$	$BaCO_3$
Volume of gas collected / cm^3	80	25	5

Using relevant data from the *Data Booklet*, explain the results obtained by the student. [3]
The ionic radius of Mg^{2+}, Ca^{2+} and Ba^{2+} are 0.065 nm, 0.099 nm and 0.135 nm respectively. Down Group 2, the ionic charge remains the same while the ionic radius increases, hence charge/size ratio decreases down the group.

Mg^{2+} has the greatest polarising power, thus it can distort the electron cloud of CO_3^{2} to a larger extent. The C O covalent bond in $MgCO_3$ is weakened more significantly and less amount of energy is required to decompose $MgCO_3$.

As a result, $MgCO_3$ decomposes more readily than $CaCO_3$ and $BaCO_3$ as it produces the largest amount of CO_2 in the same time period.

(c) Table 1.2 shows the bond length of various nitrogen-oxygen bonds.

Table 1.2

Bond	N O	N=O	nitrogen-oxygen bond in NO_3
Bond Length (nm)	0.136	0.115	0.128

Suggest an explanation for the observed NO bond length in nitrate ion. [2]
In NO_3 , the presence of continuous overlap of p orbitals across the 3 oxygen atoms and the nitrogen atom allows the □ electrons and the lone pair of electrons on oxygen to be delocalised.
As a result, all the three NO bonds in NO_3 are an intermediate bond between an N O bond and N=O bond (partial double bond) or bond order is between 1 and 2

(d) Sodium carbonate, a Group 1 carbonate, can be used to maintain the pH of swimming pool water to the ideal range of 7.0–7.6. If the concentration of sodium carbonate is too high, it will cause skin irritation to swimmers.

The management committee of a public swimming pool hired a chemist to advise them on the need to adjust the pH of pool water. The chemist titrated a 10.0 cm^3 sample of pool water (assume it contains only Na_2CO_3) against 0.05 mol dm^{-3} HC*l*.

20.00 cm^3 of the HC*l* solution was required to turn the phenolphthalein indicator from pink to colourless. When the titration is repeated using methyl orange indicator, 40.00 cm^3 of HC*l* was required to reach the end point.

[The K_{b1} and K_{b2} values of Na_2CO_3 at 25 °C are 2.13×10^{-4} and 2.25×10^{-8} respectively.]

(i) The pH at the first equivalence point is found to be greater than 7. Write an equation to explain this observed pH. [1]
$HCO_3 + H_2O \rightleftharpoons H_2CO_3 + OH$

Note: must be reversible arrow for partial dissociation of weak base.

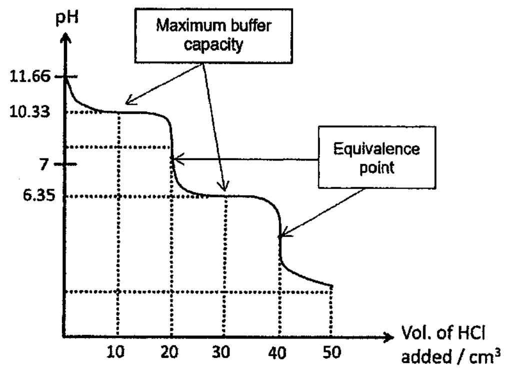
(ii) Calculate the concentration of Na_2CO_3 in the pool water sample. [1]
Working range of phenolphthalein is pH 8 10. When phenolphthalein changes colour, it indicates the first reaction between CO_3^{2} and H^+ is completed.
$CO_3^{2} + H^+$ □ HCO_3
Amount of HCl used = $\frac{20}{1000} \cdot 0.05 = 0.001$ mol
Amount of CO_3^{2} reacted = 0.001 mol
Concentration of Na_2CO_3 in 10.0 cm^3 sample = $0.001 \div \frac{10}{1000} = 0.1$ mol dm^{3}

OR
Working range of methyl orange is pH 3 5. When methyl orange changes colour, it indicates the complete reaction between CO_3^{2} and two H^+.
$CO_3^{2} + 2H^+$ □ $CO_2 + H_2O$
Amount of HCl used = $\frac{40}{1000} \cdot 0.05 = 0.002$ mol
Amount of CO_3^{2} reacted = 0.001 mol
Concentration of Na_2CO_3 in 10.0 cm^3 sample = $0.001 \div \frac{10}{1000} = 0.1$ mol dm^{3}

(iii) Using your answer to **(ii)**, calculate the initial pH of the pool water sample. [2]
$CO_3^{2} + H_2O \rightleftharpoons HCO_3 + OH$
$[OH] = \sqrt{K_b \times [CO_3^{2-}]}$
$[OH] = \sqrt{2.13 \times 10^{-4} \times 0.1}$
[OH] = 0.004615 mol dm^{3}
pOH = 2.336
pH = 14 pOH = 11.66 (2 d.p.)

allow ecf from (ii)

(iv) Sketch the pH volume added curve you would expect to obtain when 50.00 cm³ of the HC*l* solution is added to 10.0 cm³ of the pool water sample. Label the various key points on the curve. [2]



First maximum buffering capacity occurs when there is 1:1 of CO_3^{2} and HCO_3
pOH = pK_{b1}
pH = 14 – pOH = 14 –[–lg(2.13 × 10^{-4})] = 10.33 (2 d.p.)

Second maximum buffering capacity occurs when there is 1:1 of HCO_3 and H_2CO_3
pOH = pK_{b2}
pH = 14 – pOH = 14 –[–lg(2.25 × 10^{-8})] = 6.35 (2 d.p.)

Shape of pH curve
- Correct shape with 2 equivalence points
- sharp change in pH at the equivalence points
- pH is approximately constant near the point of maximum buffering capacity
- Final pH would approach low pH

Label
- Axis with units
- initial pH
- pH and volume for maximum buffer regions
- pH >7 at the first equivalence point

(e) Lithium carbonate is a sparingly soluble salt with a K_{sp} value of 8.15 × 10 ⁴.

Calculate the solubility of lithium carbonate. [2]
Let the solubility of Li_2CO_3 be s

	$Li_2CO_3(s)$	⇌	$2Li^+(aq)$	+	$CO_3^{2-}(aq)$
I /mol dm^{-3}			0		0
C /mol dm^{-3}	$-s$		$+2s$		$+s$
E /mol dm^{-3}			$2s$		s

K_{sp} of Li_2CO_3 = $[Li^+]^2[CO_3^{2-}] = (2s)^2(s)$
$8.15 \times 10^{-4} = 4s^3$
$s = 5.88 \times 10^{-2}$ mol dm ³

[Total : 19]

2 Cobalt is a *transition element* that can form coloured ions of various oxidation states in aqueous solutions.

(a) (i) Explain what is meant by the term *transition element*. [1]
Transition elements are d–block elements which form one or more stable ions with a partially filled d subshell.

(ii) Explain why aqueous solution of Co^{3+} ions is coloured. [3]
In the presence of ligands, electronic repulsion between lone pair electrons of ligands and the electrons in the 3d orbitals causes the degenerate 3d–orbitals of the Co^{3+} ions to split into two different energy levels with a (small) energy gap, ΔE. This process is called d–splitting.

As the 3d subshell is partially filled , electrons in the lower energy d orbitals can absorb light of a certain wavelength in the visible light spectrum with energy corresponding to the energy gap, ΔE, and be promoted to the higher energy 3d orbital. This process is called d–d transition.

The colour observed is the complement of the colour absorbed.

(iii) Explain why cobalt ions can exhibit variable oxidation states while calcium ion can only have oxidation state of +2. [2]
Due to the close similarity in energy of the 3d and 4s orbitals of cobalt, (different numbers of) 3d and 4s electrons can be removed to form stable ions of different oxidation states.

However, once the valence 4s electrons of calcium are removed, the subsequent electrons removed must come from the next inner quantum shell which required large additional amount of energy and hence, calcium ions does not have variable oxidation states.

BP-167

BP~168

(b) When an aqueous solution of cobalt(III) chloride, $CoCl_3$, is separately added to different amounts of aqueous ammonia under different conditions, two ionic compounds **A** and **B** are formed. Both **A** and **B** contained six–coordinated cobalt(III) complex ions containing both NH_3 and Cl^- ligands.

When excess aqueous solution of silver nitrate, $AgNO_3(aq)$, is added to one mole of **A** and one mole of **B** separately, same white precipitate is obtained. The amount of white precipitate formed is given in Table 2.1.

Table 2.1

ionic compound	amount of white ppt formed with excess $AgNO_3(aq)$
A	1 mol
B	2 mol

(i) Identify the type of reaction for the reaction between $CoCl_3$ and NH_3. [1]
Ligand exchange reaction

(ii) Identify the white precipitate. Explain why different amounts of white precipitate are formed from **A** and **B**. [2]
The white precipitate is $AgCl$.

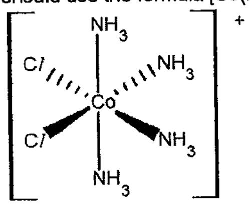
When different amounts of aqueous ammonia is added to $CoCl_3$, different number of Cl^- ligands formed coordinate bonds with Co^{3+} to form complex ions of different charges. Hence, different number of free Cl^- / counter Cl^- ions are present in A and B, resulting in different amount of $AgCl$ being precipitated out.

(iii) Deduce the formula for the **complex ions** in **A** and **B**. [2]
A: $[Co(NH_3)_4Cl_2]^+$ (1 Cl ion that can react with Ag^+, 2 Cl ligands + 4 NH_3 ligands)

B: $[Co(NH_3)_5Cl]^{2+}$ (2 Cl ion that can react with Ag^+, 1 Cl ligands + 5 NH_3 ligands)

(iv) The cobalt(III) complex ion in **A** exhibits *cis–trans* isomerism. Using your answer in **(iii)**, draw the three–dimensional structure of the *cis* isomer of **A**.

If you are unable to deduce the formula for the complex ions found in **A** in **(iii)**, you should use the formula $[Co(NH_3)_2Cl_4]^-$. This is **not** the correct answer. [1]



Note: show 2 Cl ligands side by side in 3-D octahedral complex.

(c) The reaction between iodide ions, I^-, and peroxodisulfate ions, $S_2O_8^{2-}$, in the absence of catalyst is slow. Co^{3+} ion can act as a homogeneous catalyst to speed up the reaction.

By considering suitable E° value from the ***Data Booklet***, explain how Co^{3+} functions as a catalyst for the reaction between I^- and $S_2O_8^{2-}$, writing equations where appropriate. [3]

Step 1: Formation of intermediate
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\circ = +0.54$ V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$ $E^\circ = +1.89$V

Overall: $2I^- + 2Co^{3+} \rightarrow I_2 + 2Co^{2+}$

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd} = (+1.89\text{ V}) - (+0.54) = +1.35$ V (positive, spontaneous)

Step 2: Regeneration of the catalyst
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\circ = +2.01$ V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$ $E^\circ = +1.89$ V

Overall: $2Co^{2+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Co^{3+}$

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd} = (+2.01\text{ V}) - (+1.89) = +0.12$ V (positive, spontaneous)

There is high activation energy due to the collision of two negatively–charged ions (experiencing electrostatic repulsion). This two–step reaction provides a lower energy pathway because both steps involve collision between oppositely charged ions.

(d) A series of experiments were carried out to investigate the kinetics of the uncatalysed reaction between $K_2S_2O_8$, and KI.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The initial concentrations of the $K_2S_2O_8$ and KI solutions in the mixture, and the time taken for the mixture to darken for the various experimental runs are given in Table 2.2.

Table 2.2

Experiment	Initial concentration of $K_2S_2O_8$/ mol dm^{-3}	Initial concentration of KI / mol dm^{-3}	Time taken to darken/ s
1	0.10	0.20	35
2	0.05	0.20	70
3	0.20	0.067	50
4	0.02	0.75	?

(i) Determine the rate equation for the uncatalysed reaction. [3]

Since we are monitoring time taken for a fixed amount of I_2 to be formed,

$$\text{rate} \propto \frac{1}{time\ taken}$$

Comparing expt 1 & 2, [KI] remain constant and $[K_2S_2O_8]$ × 2, rate also × 2.
Hence it is first order w.r.t $K_2S_2O_8$.

Comparing expt 1 & 3, let rate = $k[K_2S_2O_8][KI]^x$
For expt 1 : $\frac{1}{35} = k(0.10)(0.20)^x$
For expt 3 : $\frac{1}{50} = k(0.20)(0.067)^x$

Using $\frac{expt\ 3}{expt\ 1}$,
$\frac{1/50}{1/35} = \frac{k(0.20)(0.067)^x}{k(0.10)(0.20)^x}$
$0.35 = \frac{(0.067)^x}{(0.20)^x}$
Taking lg on both sides,
0.4559 = 0.4750 x
x H 1
Hence it is first order w.r.t KI.

Rate = $k[K_2S_2O_8][KI]$

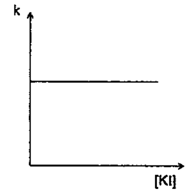
(ii) Calculate the time taken for the mixture in experiment 4 to darken. [1]

Using expt 1,
Rate = $k[K_2S_2O_8]$ [KI]
$\frac{1}{35} = k\ (0.1)(0.2)$
k = 1.429

Using the value of k for expt 4,
$\frac{1}{time\ taken} = 1.429(0.02)(0.750)$,

Time taken = 46.7s

(iii) Sketch the graph of rate constant, k, against concentration of KI at constant temperature. [1]



Note: rate constant k is only affected by temperature and catalyst.

[Total : 20]

BP-169

BP~170

3 (a) Adrenaline is both a hormone and neurotransmitter in the body. A chemistry undergraduate student has proposed to synthesise adrenaline from compound **Y** using a 3-step synthetic route as shown in Fig. 3.1.

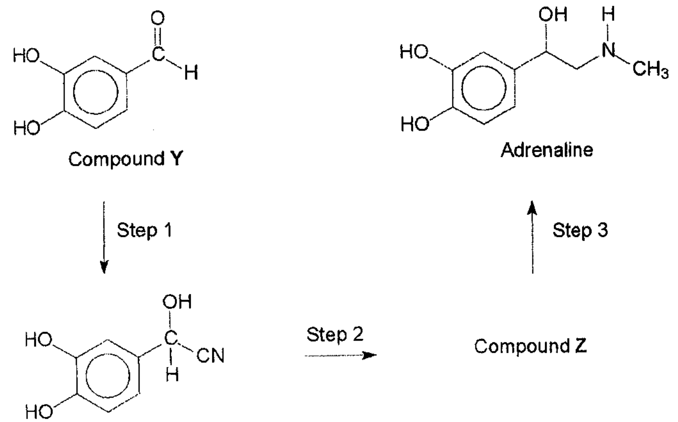


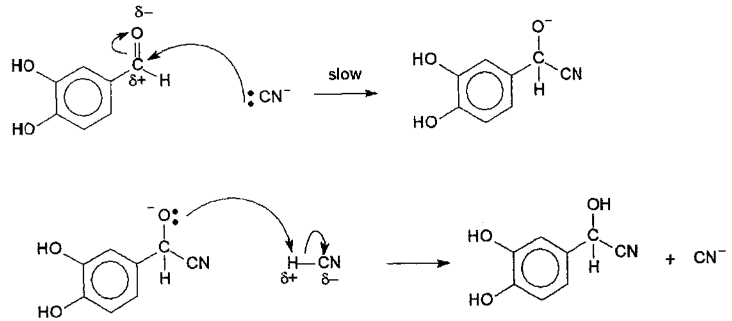
Fig 3.1

(i) State the reagent and condition for Step 1 and describe the reaction mechanism. Include all relevant lone pairs, dipoles, charges, and curly arrows. Include the structure of the organic intermediate. [4]

HCN with trace amount of NaCN OR NaOH

Nucleophilic Addition

NaCN □ Na^+ + CN

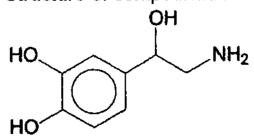


- name of mechanism
- Label partial charges, negative charge on nucleophile
- Show lone pair electron on nucleophile
- Correct use of arrow to show movement of electrons
- Correct intermediate
- Reaction with HCN to regenerate CN^-
- Label "slow" in step 1

[Turn over

(ii) Identify the structure of compound Z and state the reagents and conditions needed for Step 2 and Step 3. [3]

Structure of compound Z:



Step 2: $LiAlH_4$ in dry ether OR H_2(g), Pt(s) OR H_2(g), Ni (s) high temp & pressure

Step 3: <u>limited</u> CH_3Br, heat

Note: In step 3, compound Z acts as the nucleophile to react with CH_3Br.
With limited CH_3Br, N will be bonded to <u>ONE</u> CH_3.
With excess CH_3Br, N will be bonded to <u>THREE</u> CH_3.

(iii) Suggest how the adrenaline synthesized through the above reaction scheme is different from the naturally occurring adrenaline secreted by the adrenal glands in the body. [2]

In this reaction, a racemic mixture of adrenaline (50%: 50% of both enantiomers) is produced as Step 1 involves an attack of the CN^- on a trigonal planar C atom.

Adrenaline produced in the body is stereospecific (only one of the enantiomers is formed)

Note: It is incorrect to state that the adrenaline synthesised is the enantiomer of naturally occurring adrenaline.

Analgesics are drugs that help to relieve pain. Paracetamol and morphine are the commonly used analgesics.

(b) Fig. 3.2 shows a two-steps reaction proposed by a student to synthesize paracetamol.

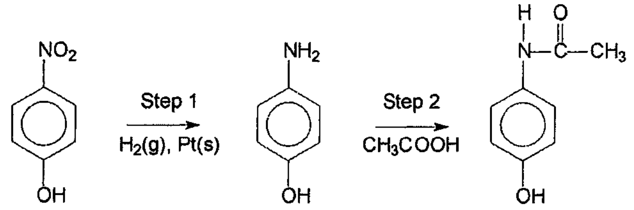


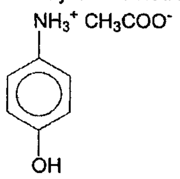
Fig. 3.2

His teacher pointed out there were mistakes in both Step 1 and 2.

(i) State the correct reagent and condition for Step 1. [1]
Sn, conc HC*l*, heat, followed by excess NaOH

(ii) Using CH_3COOH in Step 2 would produce compound **G** instead of paracetamol.

Identify the structure of compound **G**. [1]

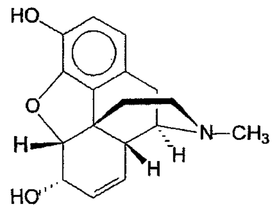


amine undergoes acid-base reaction with CH_3COOH to give salt.

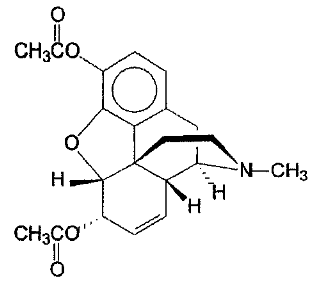
Note: No net charge for "compound". Must show both ions.

(iii) Describe the observation when neutral $FeCl_3(aq)$ is reacted with paracetamol. [1]
Violet/purple colouration

(c)



morphine



heroin

Fig. 3.3

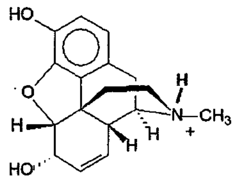
In contrast to paracetamol, narcotic analgesics such as morphine and heroin are used to relieve intense pain. Studies on the structural activity of morphine molecule has identified the three essential functional groups of morphine that bind strongly with the pain receptors and block the transmission of pain signals between brain cells are as follows:

1. Phenolic –OH group
2. Aromatic ring of phenol
3. Positively charged amine group

When injected into human body, these drug molecules need to cross the hydrophobic blood-brain barrier to reach the pain receptors. It is observed that polar molecules cross the blood-brain barrier less readily. In the brain, esterase enzymes catalyse the hydrolysis of the ester groups.

$$R\text{–}COO\text{–}R' + H_2O \rightleftharpoons RCOOH + R'\text{–}OH$$

(i) In the physiological pH of 7.4, the tertiary nitrogen atom of morphine and heroin is protonated. On Fig. 3.3, complete the structure to show the protonated form of morphine. [1]



(ii) Suggest why heroin shows greater pain-relieving effect than morphine despite lacking the essential phenolic –OH group to bind with the pain receptors. [2]
Heroin is a less polar molecule than morphine, and it is able to pass the predominantly non-polar blood-brain barrier more readily than morphine molecule.

In the brain, the heroin molecule undergoes hydrolysis by esterase enzymes to produce the morphine molecule which would have the essential phenolic –OH group to bind with the pain receptors.

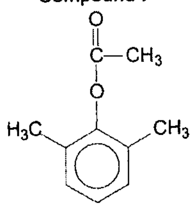
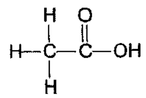
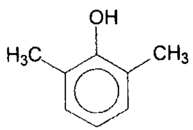
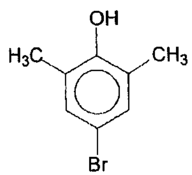
BP-171

BP-172

(d) Compound **P**, $C_{10}H_{12}O_2$, reacts with hot H_2SO_4(aq) to give compound **Q**, $C_2H_4O_2$, and compound **R**, $C_8H_{10}O$. Compound **R** reacts with Br_2(aq) to gives compound **S**, C_8H_9OBr, a symmetrical molecule.

Suggest possible structures for **P**, **Q**, **R**, **S**. For each reaction, state the type of reaction described and make deductions about the functional groups present. [6]

P undergoes **acidic hydrolysis** with hot H_2SO_4(aq). **Ester** is present in **P**.
Q contains a **carboxylic acid** and **R** contains **alcohol/phenol**
R undergoes **electrophilic substitution** (1 H atom of R is replaced by 1 Br atom in S) with Br_2(aq). **R** contains **phenol**.
Phenol with Br_2(aq) usually gives tri-substitution at position 2,4,6 of phenol. However since only 1 Br is substituted on the phenol, two of the 2,4,6 position must be occupied by side chain.
Since **S** is a symmetrical molecule, the two side chains must be at position 2 and 6 of phenol.

Compound **P**	Compound **Q**
	
Compound **R**	Compound **S**
	

Common mistakes:
Some students wrongly classify reaction of **P** with hot H_2SO_4(aq) as oxidation of alkene. Vigorous oxidation of alkene requires strong oxidizing agent, $KMnO_4$.

Some students wrongly classify reaction of **R** with Br_2(aq) as electrophilic substitution of benzene. Benzene requires anhydrous $FeBr_3$ catalyst and Br_2 for electrophilic substitution. Phenol, with strongly activating OH attached to benzene, can undergo electrophilic substitution more readily with Br_2(aq), without catalyst.

[Total : 21]

Section B

Answer **one** question from this section.

4 A strip of iron metal was reacted until completion with an excess of hot concentrated sulfuric acid. A pale-green solution **J** that contained only Fe^{2+}(aq) ions was obtained and effervescence of SO_2 was also observed.

(a) (i) Construct the balanced equation for the reaction between Fe(s) and hot concentrated H_2SO_4. [1]

[R] $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$
[O] $Fe \rightarrow Fe^{2+} + 2e^-$

Overall eqn: $Fe + SO_4^{2-} + 4H^+ \rightarrow Fe^{2+} + SO_2 + 2H_2O$

(ii) The E°_{cell} for this reaction is +0.61 V. Give two reasons why an equilibrium mixture is not produced when iron reacts with an excess of hot concentrated sulfuric acid. [3]

Any 2 points:

1. Positive E°_{cell} shows that the reaction is spontaneous and the formation of product is favoured. Equilibrium is usually for redox reactions with $E^\circ_{cell} = 0$.

2. This is not a closed system. SO_2(g) produced is allowed to escape from the reaction system. Equilibrium state cannot be achieved.

3. $SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O \quad E^\circ = +0.17$ V

   The E° is given under standard conditions of 298 K and concentrations of all aqueous ions at 1 mol dm^{-3}.

   When concentrated H_2SO_4 is used, the **concentration of SO_4^- and H^+ are greater than 1 mol dm^{-3}**. This increase in concentration would **shift the position of equilibrium to the right**, (favouring reduction), **increasing the E value for this half cell** and hence causing **E_{cell} to become more positive**. The overall redox reaction would favour the formation of products when concentrated H_2SO_4 is used, the reaction is unlikely to be an equilibrium mixture.

(b) Solution **J** was cooled and an aliquot was mixed with an excess of acidified potassium iodate(V), KIO_3.

The overall stoichiometry of the reaction taking place in the conical flask is

$$10Fe^{2+}(aq) + 2IO_3^-(aq) + 12H^+(aq) \rightarrow 10Fe^{3+}(aq) + I_2(aq) + 6H_2O(l)$$

All of the liberated iodine was titrated with standard aqueous sodium thiosulfate.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

In one titration, a 25.0 cm^3 aliquot of **J** requires 18.60 cm^3 of 0.150 mol dm^{-3} $Na_2S_2O_3(aq)$ to reach the end-point.

Calculate the molar concentration of Fe^{2+} in solution **J**. [2]

Amount of $S_2O_3^{2-} = \frac{18.60}{1000} \times 0.150$
$= 0.00279$ mol

$S_2O_3^{2-} : I_2 = 2 : 1$

Amount of $I_2 = \frac{1}{2} \times 0.00279 = 0.001395$

$I_2 : Fe^{2+} = 1 : 10$

No. of mol of $Fe^{2+} = 10 \times 0.001395$
$= 0.01395$ mol

$[Fe^{2+}]$ in solution **J** $= \frac{0.01395}{\frac{25.0}{1000}} = 0.558$ mol dm^{-3}

[Turn over

(c) Liberated iodine is kept dissolved in solution by a large excess of iodide via the equilibrium:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K_c = 7.1 \times 10^2 \text{ mol}^{-1}\text{dm}^3$$

Just before the end-point of the titration, the combined iodine concentration, $[I_2] + [I_3^-]$, is about 1.0×10^{-4} mol dm^{-3}, while the iodide concentration remains at 0.10 mol dm^{-3}.

(i) Write the K_c expression for the equilibrium. [1]

$K_c = \frac{[I_3^-]}{[I_2][I^-]}$

(ii) Using these data and the K_c expression for the equilibrium, calculate the concentration of free iodine, $[I_2]$, present at this stage of the titration. [2]

Given $[I_2] + [I_3^-] = 1.0 \times 10^{-4}$
$[I_3^-] = 1.0 \times 10^{-4} - [I_2]$ -- (1)

$K_c = \frac{[I_3^-]}{[I_2][I^-]} = 7.1 \times 10^2$ -- (2)

Substituing eqn 1 into eqn 2:

$\frac{1.0\times10^{-4} - [I_2]}{[I_2][I^-]} = 7.1 \times 10^2$

$\frac{1.0\times10^{-4} - [I_2]}{[I_2](0.10)} = 7.1 \times 10^2$

$72\,[I_2] = 1 \times 10^{\ 4}$

$[I_2] = 1.39 \times 10^{-6}$ mol dm^{-3}

(iii) Hence determine the percentage of the total iodine present as *free* I_2. [1]

% of free $I_2 = \frac{1.39 \times 10^{-6}}{1.0\times10^{-4}} \times 100$
$= 1.39\%$

Note: It is given that total iodine concentration, $[I_2] + [I_3^-]$, $= 1.0 \times 10^{-4}$ mol dm^{-3}

(d) Describe and explain the trend in the thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. [3]

$2HX \rightarrow H_2 + X_2$

H–X bond is broken during the thermal decomposition of H-X. Down the Group, bond energy of H–X decreases from H–C*l* (431 kJ mol^{-1}) to H–I (299 kJ mol^{-1}), and less energy is needed to overcome the H–X bond.

Thus, the thermal stability of the hydrogen halides decreases down the Group.

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(e) Three pure solid component labelled **D**, **E** and **F** are placed on the lab bench. It is known that the compounds are $AlCl_3$, Na_2CO_3 or $MgSO_4$.

A student performed several tests, and the results are summarised in Table 2.3.

Table 2.3

Compound	pH of the aqueous solution of the compound	results of adding NaOH(aq) to a solution of the compound	results of adding HC*l*(aq) to the solid compound
D	> 7	No observed reaction	Evolution of a gas
E	< 7	White ppt soluble in excess NaOH	No observed reaction
F	< 7	White ppt insoluble in excess NaOH	No observed reaction

(i) Suggest the identity of Compound **D**, **E** and **F** based on the observations in Table 2.3. [2]
Compound D : Na_2CO_3
Compound E : $AlCl_3$
Compound F : $MgSO_4$

(ii) Suggest the formula of the white compound observed when an excess of NaOH is added to a solution of the compound **F**. [1]
$Mg(OH)_2$

(iii) With the aid of an equation, explain why an aqueous solution of **E** has a pH < 7. [2]
$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

Al^{3+} has a **high** $\frac{charge}{size}$, it **<u>polarise and weaken the O-H covalent bond in H_2O to a large extent</u>** and causes one of the six H_2O in $[Al(H_2O)_6]^{3+}$ to dissociate into H^+ and OH^-. $[Al(H_2O)_5()]^{2+}$ is produced and **<u>H^+(aq) is released</u>** into the solution during **<u>hydrolysis.</u>**

(f) Beryllium oxide, BeO, has similar chemical properties as Al_2O_3.

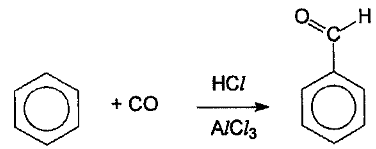
Write the chemical equations when separate samples of BeO are reacted with HC*l*(aq) and NaOH(aq). [2]
$BeO + 2HCl$ ↓□ $BeCl_2 + H_2O$

$BeO + 2\,NaOH + H_2O$ ↓□ $Na_2[Be(OH)_4]$
Accept ionic equations

[Total : 20]

[Turn over

5 (a) Benzaldehyde, C_6H_5CHO, served as a precursor in the production of various chemicals, including pharmaceuticals and dyes. Benzaldehyde can be synthesised from carbon monoxide and benzene by the Gatterman–Koch reaction in the presence of hydrogen chloride and aluminium chloride. This reaction is an electrophilic substitution reaction.



The following describes the mechanism for the reaction.

step 1: Carbon monoxide, hydrogen chloride and aluminium chloride reacts to form the electrophile, $H-\overset{+}{C}=O$, and one other product.

step 2: The electrophile reacts with benzene to form an intermediate in the rate–determining step.

step 3: The intermediate loses a H^+ to regenerate hydrogen chloride and aluminium chloride.

(i) Explain why benzene undergoes substitution reactions rather than addition reaction. [1]

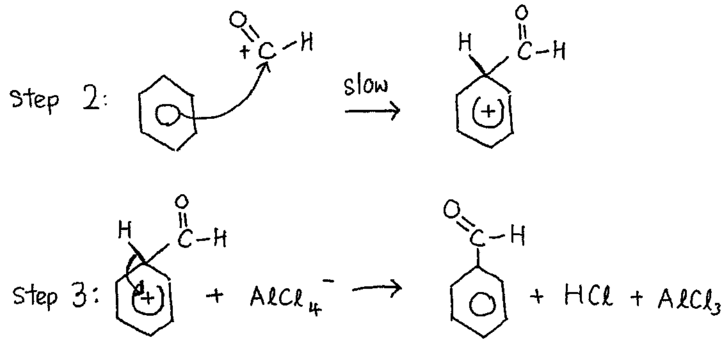
The ring of delocalised π electrons give benzene additional resonance stability. <u>Addition reaction destroys this resonance stability</u> and hence it is not favoured. Instead, benzene undergoes <u>substitution reaction to maintain this resonance stability</u>.

(ii) Write the equation for the generation of the electrophile in step 1 of the Gatterman–Koch reaction. [1]

$CO + HCl + AlCl_3 \rightarrow H-\overset{+}{C}=O + AlCl_4^-$

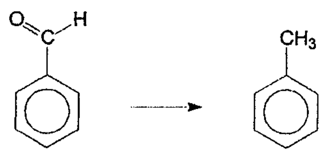
(iii) $AlCl_3$ acts as a ***Lewis acid*** in step 1 of the reaction. Describe how $AlCl_3$ act as a *Lewis acid* in this step. [1]
$AlCl_3$ acts as a Lewis acid as it can <u>accept the lone pair electrons</u> from C*l* in HC*l*.

(iv) Draw a reaction mechanism for step 2 and step 3. Include all relevant charges and curly arrows. Include the structure of the organic intermediate. [2]



- Label positive charge on electrophile
- Label "slow" in step 2
- Correct use of arrow to show movement of electrons
- Correct intermediate with "opening" and positive charge.
- Break C H to regenerate aromatic ring
- Show balanced equation in regenerating HC*l* and A*l*C*l*$_3$

(v) Benzaldehyde formed can undergo further reaction to form methylbenzene.



State the type of reaction that benzaldehyde undergoes and explain your answer. [2]
Reduction reaction. This is because there is gain of hydrogen atoms/ loss of oxygen atoms by benzaldehyde.

(b) The concentration of chromium(VI) in aqueous solution may also be determined using a colorimeter.

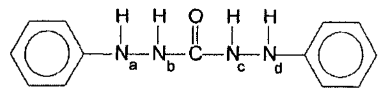
On adding 1,5-diphenylcarbazide, DPC, to a solution of chromium(VI) ions, an intensely coloured octahedral complex is formed. The formula of the complex is $[Cr(DPC)_3]^{6+}$.

(i) The coordination number of the complex, $[Cr(DPC)_3]^{6+}$ is 6.

Explain what is meant by *coordination number* for the complex, $[Cr(DPC)_3]^{6+}$. [1]
It is the number of co-ordinate bonds (dative bonds) that the central metal ion, Cr^{6+}, formed with DPC ligands.

[Turn over

(ii) The structure of DPC is shown.



DPC is able to act as a bidentate ligand using lone pair electrons on N_a and N_d. Explain why the lone pair electrons on N_b and N_c are not available. [1]
Lone pair electrons on N_b and N_c are significantly delocalised to the adjacent C=O with highly electronegative O atom.

(iii) Suggest why the intense colour of the complex, $[Cr(DPC)_3]^{6+}$, is not due to the movement of electrons between split d-orbitals in the chromium ion. [1]
Cr^{6+} has an empty d subshell hence there is no d-splitting and d-d transition.

(c) Potassium dichromate(VI), $K_2Cr_2O_7$, is present in very small amounts in cement, to help increase the time for the cement to set.

A 50.0 g sample of cement was washed with portions of deionised water to dissolve the potassium dichromate(VI). Any insoluble residues were removed by filtration and the filtrate was transferred to a volumetric flask. The volume was made up to 100.0 cm^3 using 2.0 mol dm^{-3} sulfuric acid.

50.0 cm^3 of this solution was transferred to a conical flask and titrated with a solution of ammonium iron(II) sulfate, $(NH_4)_2Fe(SO_4)_2$, of concentration 3.24×10^{-4} mol dm^{-3}. The following reaction occurs.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The indicator *N*-phenylanthranilic acid was used, which gave an intense red-violet colour at the end-point.

The mean titre of ammonium iron(II) sulfate was 10.90 cm^3.

(i) Suggest a reason why an indicator is necessary in this titration. [1]
The colour change from orange to green at the end-point is not distinctive / not sharp enough / not easy to detect (without an indicator).

(ii) Calculate the percentage by mass of potassium dichromate(VI) in the cement sample. [3]

Amt of $(NH_4)_2Fe(SO_4)_2 = \frac{10.90}{1000} \times 3.24 \times 10^{-4}$
$= 3.532 \times 10^{-6}$ mol

Amt of $Cr_2O_7^{2-}$ (in 50.0 cm^3) $= \frac{1}{6} \times 3.532 \times 10^{-6}$
$= 5.886 \times 10^{-7}$ mol

Amt of $Cr_2O_7^{2-}$ (in 100.0 cm^3) $= 2 \times 5.886 \times 10^{-7} = 1.177 \times 10^{-6}$ mol

Mass of $K_2Cr_2O_7$ in sample $= 1.177 \times 10^{-6} \times (2 \times 39.1 + 2 \times 52.0 + 7 \times 16.0)$
$= 1.177 \times 10^{-6} \times 294.2$
$= 3.463 \times 10^{-4}$ g

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% by mass of $K_2Cr_2O_7$ in 50.0 g sample = $\frac{3.463 \times 10^{-4}}{50.0} \times 100$
= 6.925×10^{-4} %

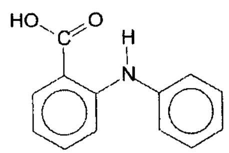
(iii) Potassium dichromate(VI) can cause allergic contact dermatitis in some individuals. Regulations have been put in place in some countries to limit the content of potassium dichromate(VI) in cement to no more than 2mg per kg of cement.

Using your answer in **(ii)**, determine if the 50.0 g sample of cement is safe for usage. [2]

% by mass of safe limit = $\frac{2 \times 10^{-3}}{1000} \times 100\% = 2 \times 10^{-4}$ % by mass

Since the sample contains 6.93×10^{-4} % of $K_2Cr_2O_7$ by mass, it exceeds the safe limit and is not safe for usage.

(d) *N*-phenylanthranilic acid has the structure shown below.

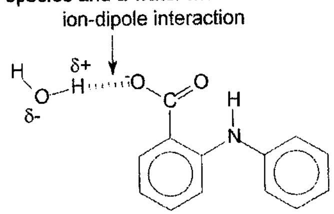


(i) Explain why *N*-phenylanthranilic acid has low solubility in water. [1]
N-phenylanthranilic acid contains two benzene rings. Energy released in the formation of instantaneous dipole-induced dipole interactions between the benzene rings of *N*-phenylanthranilic acid molecules and water molecules is insufficient to overcome the hydrogen bonds between water molecules and the hydrogen bonds between *N*-phenylanthranilic acid molecules.

To use *N*-phenylanthranilic acid as an indicator for the reaction described in **(c)**, it is first mixed with sodium hydroxide, NaOH(aq).

(ii) State the type of reaction between *N*-phenylanthranilic acid and NaOH(aq). [1]
Acid-base reaction.

(iii) Draw a labelled diagram to illustrate the interaction between the resultant organic species and a water molecule. [2]



Also accept hydrogen bond (then lone pair on O^- needs to be shown)

[Total : 20]